Reduction of Membrane Fouling in Membrane Bioreactors - Development of Innovative and Sustainable Techniques

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ABSTRACT

Over the past decade, membrane technology has become a worldwide implemented, acknowledged separation process. Although membrane bioreactors (MBRs) still require further research efforts regarding operating and economic efficiency, they offer considerable advantages compared to conventional activated sludge systems, such as smaller foot print, modular construction, and superior effluent quality. They are especially preferred in cases where stringent water quality requirements have to be guaranteed.

One of the main challenges in the operation of MBRs is membrane fouling, causing flux decrease and the increase of the transmembrane pressure. Its control and prevention result in high manpower requirements as well as in increased electrical power consumption and the need for cleaning chemicals. Therefore, most MBR researches aim to identify, investigate, and control membrane fouling.

The research on fouling reduction and permeability loss in MBRs was carried out at three MBR pilot plants with synthetic and real wastewater. On the one hand, the effect of mechanical cleaning with an abrasive granular material on the performance of a submerged MBR process was tested. Additionally, scanning electron microscopy (SEM) measurements and integrity tests (rejection measurements and water microbiology testing) were conducted to check whether the membrane material was damaged by granulates.

The results indicate that the fouling layer formation was significantly reduced by abrasion using the granular material. This technique allowed a long-term operation of more than 600 days at a flux up to 40 L/(m^2·h) without chemical cleaning of the membranes. However, at high flux rates (> 35 L/(m^2·h)) a significant decline in permeability was observed, presumably as a result of permeation drag forces that might draw the particulate and colloidal matter towards the membrane surface.

It was demonstrated that the MBR with granulate could be operated with more than 27 % higher flux compared to conventional MBR operation. SEM images and integrity tests showed that in consequence of abrasive cleaning, the granular material left brush marks on the membrane surface; however, the membrane function was not affected. Rejection measurements indicated no damaging effects by granulate, as the rates were comparable with those of new membranes (> 90 %). Water microbiology testing (removal of E. coli and total coliforms) showed that granulate did not have any negative impact on the membranes and still rejected almost all bacteria in the system.

Additionally to the experiments with granulate, the impact of membrane backwash, using a salt brine solution, the impact of chemical and physical cleaning (relaxation breaks), and the effect of changed milieu conditions (aerobic, anaerobic) on membrane fouling was investigated. Among the chemical and physical methods relaxation breaks have proved to enhance membrane performance; however, this involves high specific costs due to operation interruptions, i.e. low membrane throughput.

Research on permeability loss was carried out to investigate the influence of operating conditions (temperature, sludge retention time/sludge loading, and wastewater composition) and the influence of activated sludge characteristics (mixed liquor suspended solids, colloidal matter, truly soluble matter, viscosity) on fouling. It was shown that the concentration of the colloidal fraction obviously depends on the operating temperature and sludge retention time (SRT). A nearly linear correlation between the colloidal fraction ($COD_{colloidal}$) and the concentration of biopolymers (proteins and polysaccharides) was found. However, while a relationship between the retention of biopolymers and capillary suction time (CST) of activated sludge was found, a clearly connection with the permeability of the investigated membranes did not exist. It was observed that the addition of polyaluminum chloride coagulant

resulted in the reduction of the colloidal fraction in the supernatant by up to 80 % of the initial value. The coagulant even bound soluble matter < 0.04 μm, as the chemical oxygen demand (COD) concentration of permeate was slightly higher.

Fractionation tests showed that the colloidal fraction (0.04-0.1 μm) constituted the largest percentage of COD (71 %) and dissolved organic carbon (DOC) (81 %) of samples during high fouling in the MBR, whereas this fraction made up only 21 % (COD) and 20 % (DOC) of samples during low fouling. It was observed that the biological degradation of organic matter was much higher during periods of low fouling and only 41 % of organic compounds were retained by the membrane in the reactor compared to 84 % during periods of high fouling. This implies that most of the biopolymers (proteins, polysaccharides) were retained in the reactor by membrane separation.

In a parallel experimental set up, the impact of the operationally fraction < 0.04 μm from wastewater and activated sludge on the ultrafiltration membrane fouling characteristics was investigated. Hereby, the fraction < 0.04 μm was defined operationally as the “truly soluble fraction”, determined by the separation abilities of the applied membrane. It was shown that the permeability loss was caused predominantly by the colloidal fraction > 0.04 μm rather than by the dissolved fraction of wastewater and activated sludge.

The rheological measurements showed a structural viscous behavior of the investigated activated sludge samples. Moreover, it was found that with increasing mixed liquor suspended solids (MLSS) concentration, the viscosity also tends to increase. The viscosity amounted to 18 mPa·s at a “common” MLSS concentration of 12 g/L in MBRs and a shear rate of 40 s^{-1}. A correlation between the apparent viscosity and the retention of proteins and polysaccharides in the mixed liquor filtrate of activated sludge was observed. The coefficients of both model approaches (Oswald de Waele and Herschel-Bulkley) could be described as a function of MLSS concentration using a non-linear regression analysis, however the Oswald de Waele approach showed a better plausibility with the measured values.

It was demonstrated that the energy consumption of the coarse-bubble crossflow system for fouling control is about two times higher than the fine-bubble crossflow system for oxygen supply.

ZUSAMMENFASSUNG

Im vergangenen Jahrzehnt ist die Membrantechnologie zum weltweit eingesetzten und anerkannten Trennverfahren geworden. Obwohl das Membranbelebungsverfahren (MBR - Membran-Bio-Reaktor) nach wie vor Weiterentwicklung bezüglich der Leistungsfähigkeit und der Wirtschaftlichkeit benötigt, bieten die MBR-Anlagen beträchtliche Vorteile gegenüber konventionellen Belebungsverfahren. Vor allem sind der geringe Platzbedarf, der modulare Aufbau und die hervorragende Ablaufqualität durch den vollständigen Feststoff und Bakterienrückhalt zu nennen. MBR-Anlagen werden insbesondere dort bevorzugt eingesetzt, wo strengste Anforderungen an die Wasserqualität erfüllt werden müssen.

Die zentrale Herausforderung dieser Verfahrenstechnik ist das Membranfouling, da dieses den Durchsatz verringert. Die Maßnahmen zur Begrenzung des Foulings führen zu erhöhtem Energie-, Personal-, und Chemikalienbedarf und somit zu erhöhten Betriebskosten. Zahlreiche Forschungsgruppen setzen sich deshalb mit dem Membranfouling auseinander, um die Natur des MBR-Foulings zu verstehen.

Die Untersuchungen zur Prävention des Foulings und zum Permeabilitätsverlust bei Membranbioreaktoren wurden auf drei MBR-Versuchsanlagen mit synthetischem und realem Abwasser durchgeführt.

In erster Linie wurde die Reduzierung des Membranfoulings durch die Zugabe von abrasiv wirkenden Granulaten im Belebtschlamm getestet. Zudem wurden die Aufnahmen mit Rasterelektronenmikroskop (REM) und die Integritätstests (Rückhaltemessungen, mikrobiologische Tests) zur Bewertung des Einflusses der Abrasion durchgeführt. Die Ergebnisse haben gezeigt, dass die mechanische Reinigung durch die Zugabe von Granulaten die ungewünschte Deckschichtbildung durch Abrasion verringert werden konnte. Mit dieser Methode wurde ein kontinuierlicher Betrieb ohne chemische Reinigungen und zugleich bei sehr hohen spezifischen Flüssen bis zu 40 L/(m^2·h) über mehr als 600 Betriebstage aufrechterhalten. Erst bei höheren Flüssen (> 35 L/(m^2·h)) wurde eine signifikante Abnahme der Permeabilität beobachtet. Dies deutet darauf hin, dass während der Hochlastphase mit Flüssen zwischen 35 und 40 L/(m^2·h) ein irreversibles Fouling, vermutlich wegen der „Schleppkraft der Filtratströmung“, die die kolloidalen und partikulären Stoffe zur Membranoberfläche transportiert, stattgefunden hat. Ein wirtschaftlicher MBR Betrieb mit Granulaten gegenüber konventionellen MBR Verfahren konnte mit einer 27 %igen Steigerung des Flusses nachgewiesen/realisiert werden. Die REM-Aufnahmen und die Integritätstests haben gezeigt, dass die Granulate auf der Membranoberfläche die Reinigungsspuren hinterlassen haben, allerdings nur geringe Oberflächenverletzungen festzustellen waren und die Membran intakt blieb, da ähnliche Rückhalte wie bei neuen Membranen (> 90 %) erzielt wurden und fast alle Bakterien durch die Membran zurückgehalten werden konnten.

Zusätzlich zu den Untersuchungen mit Granulaten wurde der Einfluss der Permeatrückspülungen mit einer Solelösung, der Einfluss der physikalischen (Filtrationspausen) und chemischen Reinigung sowie die Auswirkung des biologischen Milieuwechsels (aerob, anaerob) auf die Minimierung des Foulingprozesses untersucht. Unter den chemischen und physikalischen Methoden erwiesen sich die Filtrationspausen (Relaxationen) als Maßnahme zum Erhöhen der MBR-Performance als erfolgreichste. Die Relaxationen sind allerdings mit hohen spezifischen Kosten durch die Betriebsunterbrechungen bzw. geringen Membrandurchsätze verbunden.

Darüber hinaus wurden Untersuchungen zum Permeabilitätsverlust bei Membranbioreaktoren durchgeführt, wo die Betriebsbedingungen (Temperatur, Schlammalter/Schlammbelastung, Abwasserzusammensetzung) und der Einfluss der Schlammeigenschaften (TS-Gehalt, kolloidale Stoffe, gelöste

Stoffe, Viskosität) auf das Fouling getestet wurden. Einige Parameter sind eng miteinander verknüpft und lassen sich nicht unabhängig variieren.

Es wurde gezeigt, dass die Konzentration der Kolloidfraktion (0,45-0,04 μm) offenbar von Temperatur und Schlammalter abhängt. Sie scheint bei niedriger Temperatur anzusteigen. Parallelmessungen der Protein- und Polysaccharidkonzentrationen (Biopolymere) belegen einen nahezu linearen Zusammenhang mit dem kolloidalen CSB. Während ein Zusammenhang zwischen dem Rückhalt an Proteinen und Polysacchariden mit der CST (capillary suction time – kapillare Fließzeit) des Belebtschlamms festgestellt werden konnte, ist ein eindeutiger Zusammenhang mit der Permeabilität der Membranen nicht gegeben. Zusätzlich wurde beobachtet, dass die Zugabe vom Polyaluminiumchlorid-Fällungsmittel eine Abnahme der Kolloidfraktion in der Wasserphase des Belebtschlamms um bis zu 80 % des Anfangswertes ergab. Das Fällungsmittel konnte ebenfalls gelöste Stoffe kleiner als 0,04 μm binden, da die CSB-Konzentration im Permeat etwas höher lag als in der Wasserphase des Belebtschlamms.

Fraktionierungsversuche zeigten, dass die Kolloidfraktion (0,04-0,1 μm) während des hohen Foulingpotenzials der MBR-Anlage den größten Anteil in der Wasserphase des Belebtschlamms darstellte, ausgedrückt als CSB (71 %) und DOC (81 %) Konzentration. Diese Fraktion machte nur 21 % (CSB) und 20 % (DOC) der untersuchten Proben während des niedrigen Foulingpotenzials in der MBR-Anlage aus. Zudem wurde beobachtet, dass der biologische Abbau organischer Inhaltsstoffe in Zeiten des geringen Foulingpotenzials (41 %iger Rückhalt der organischen Stoffe durch die Membran) wesentlich höher war als in Zeiten des hohen Foulingpotenzials (84 %). Dass bedeutet auch, dass der größte Teil der Biopolymere (Proteine, Polysaccharide) im Reaktor durch die Membran zurückgehalten wurden.

In der weiteren Untersuchung zum Einfluss der durch die Membrantrenngrenze definierten gelösten Stoffe (< 0,04 μm) auf das Foulingsverhalten wurde festgestellt, dass der Permeabilitätsverlust überwiegend von „partikulären“ Abwasser- und Belebtschlammstoffen größer 0,04 μm hervorgerufen wurde.

Aus den rheologischen Untersuchungen ergab sich, dass der untersuchte Schlamm der Membranbelebungsanlage ein strukturviskoses Fließverhalten aufweist, d.h. bei steigender Scherbeanspruchung reduziert sich die Viskosität. Es wurde festgestellt, dass mit steigenden Trockensubstanzgehalten die Viskosität tendenziell ansteigt. Bei „üblichen“ Trockensubstanzgehalten von 12 g/L in Membranbelebungsanlagen und einer Scherrate von 40 s^{-1} liegt die Viskosität etwa bei 18 mPa·s. Zudem konnte festgestellt werden, dass die Viskosität bei einer Scherrate von 40 s^{-1} abhängig von der Menge an zurückgehaltenen Polysacchariden und Proteinen im filtrierten Schlammwasser ist. Die Koeffizienten der beiden Modellierungsansätze (Oswald de Waele, Herschel-Bulkley) ließen sich als Funktion der Trockensubstanz mit Hilfe der nicht-linearen Regressionsanalyse beschreiben. Allerdings zeigte der Ansatz nach Oswald de Waele eine bessere Übereinstimmung mit den gemessenen Daten.

Weiterhin konnte gezeigt werden, dass der Energiebedarf des mittelblasigen Crossflow-Belüftungssystems zur Foulingkontrolle mehr als doppelt so hoch ist als für das feinblasige Crossflow-System zur Sicherstellung der Sauerstoffversorgung der Mikroorganismen.

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Darmstadt, 2011

Barbara Siembida-Lösch

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SYMBOLS AND ABBREVIATIONS

Latin symbols

a - adhesive distance (0.4 nm)
a, b, c, d - constants, [-]
A_M - area of membrane, [m^2]
$BOD_{5,inf}$ - concentration of BOD_5 in influent, [mg/L]
c - solute concentration, [mol/L, kg/m^3]
c_b - bulk concentration, [mg/L]
c_g - gel concentration, [mg/L]
$c_{i,F}$ - concentration of component i in feed, [mg/L, mol/L]
$c_{i,P}$ - concentration of component i in permeate, [mg/L, mol/L]
c_m - concentration at the membrane surface, [mg/L]
c_N - concentration “N” in the sample, [mg/L]
c_s - DO saturation concentration, [mg/L]
c_x - DO concentration, [mg/L]
CFV - crossflow velocity, [m/s]
COD_{inf} - concentration of COD in influent, [mg/L]
CST - capillary suction time, [s]
dc/dx - concentration gradient in the laminar boundary film layer, [$kg/(m^3 \cdot m)$]
d - granulate diameter, [m]
d_p - sphere diameter, [m]
d_{pore} - diameter of the capillaries, [m]
d_h - hydraulic mean diameter of the feed channel, [m]
D - diffusion coefficient, [m^2/s]
DM - dry matter, [g/L]
F_D - crossflow drag force, [N]
F_F - friction force, [N]
F_L - lift force, [N]
F_{vdw} - van der Walls force, [N]
F_Y - drag force of the filtrate flow, [N]
h_d - immersion depth of diffuser, [m]
h_ϖ - Lifschitz-van der Waals constant, [eV]
HRT - hydraulic retention time, [h]
J - permeate flux rate, [$L/(m^2 \cdot h)$]
J_p - volumetric flux, [$L/(m^2 \cdot h)$, m/s]
k - mass transfer coefficient, [m/s]
k_B - Boltzmann constant ($1.3807 \cdot 10^{-23}$), [J/K]
k_La - apparent volumetric mass transfer coefficient, [1/h]
K - constant equal to 2 for perfectly cylindrical pores, [-]
K_c - consistency factor, [$Pa \cdot s^n$]
l_c - length of the capillaries, [m]
L - length of the feed channel, [m]
L_p - permeability, [$L/(m^2 \cdot h \cdot bar)$]
MLSS - mixed liquor suspended solids, [g/L]

MLVSS - mixed liquor volatile suspended solids, [g/L]
MW - molecular weight, [Da]
MWCO - molecular weight cut-off, [Da]
n - flow index, [-]
N - accumulation factor, [-]
p - pressure, [bar]
p_C - pressure on the concentrate side, [bar]
p_F - pressure on the feed side, [bar]
p_P - pressure on the permeate side, [bar]
Δp - transmembrane pressure (TMP), [bar]
P - energy demand for oxygen transfer, [Wh/(m^3·m)]
P_p - permeability constant, [m/(Pa·s)]
$P_{x,d}$ - daily sludge production, [kg/d]
$q_3(x)$ - particle size distribution, [%]
R - rejection rate, [%]
R_a - adsorption resistance, [1/m]
R_c - cake resistance, [1/m]
R_{cp} - concentration polarization resistance, [1/m]
Re - Reynolds number, [-]
R_f - fouling resistance, [1/m]
R_g - gel layer formation resistance, [1/m]
R_m - resistance of the membrane, [1/m]
R_p - pore blocking resistance, [1/m]
R_t - total filtration resistance, [1/m]
S - specific area (surface area per unit volume), [m^2/m^3]
SAD_m - specific aeration demand per membrane area, [$m^3/(m^2 \cdot h)$]
SAD_p - specific aeration demand per permeate volume, [$m^3/(m^3 \cdot h)$]
SAE - standard aeration efficiency, [kg O_2/kWh]
Sc - Schmidt number, [-]
sEPS - soluble extracellular polymeric substances, [mg/L]
SLR - sludge loading rate, [kg/(TSS·d)]
SMP - soluble microbial products, [mg/L]
SOTE - standard oxygen transfer efficiency, [%]
SOTR - standard oxygen transfer rate, [kg O_2/h]
SRT - sludge retention time, [d]
SS - suspended solids, [g/L]
SSOTE - specific standard oxygen transfer efficiency, [%/m]
SSOTR - specific standard oxygen transfer rate, [g/(m^3·m)]
SVI - sludge volume indices, [mL/g]
t - operation time, [h]
T - temperature, [°C]
TOC - total organic carbon, [mg/L]
TSS - total suspended solids, [g/L]
Q - flow rate, [m^3/d]
Q_f - air flow rate, [m^3/h]
Q_w - waste sludge flow rate, [m^3/d]

v_F - filtration rate, filtration flow, flux, [$m^3/(m^2 \cdot h)$]
V - reactor volume, [m^3]
V_i - initial volume (supernatant), [m^3]
VLR - volumetric loading rate, [$kg/(m^3 \cdot d)$]
VSS - volatile suspended solids, [g/L]
V_N - volume "N" (accumulated supernatant $V_N = V_{initial} - V_{permeate}$), [$m^3$]
V_p - volume of permeate, [L]
x - particle size, [m]
X - biomass concentration, [g/L]
X_e - concentration of biomass in effluent, [g/L]
X_{MC} - sludge concentration in the membrane chamber, [g/L]
X_R - concentration of biomass in return flow, [g/L]
y - distance to the membrane, [mm]

Greek symbols

α - relative oxygen transfer ratio, [-]
δ_l - thickness of the laminar boundary film layer, [m]
δ_p - thickness of the porous layer, [m]
ε - porosity (or voidage), [-]
η - permeate dynamic viscosity, [Pa·s]
ρ - density, [kg/m^3]
φ - specific packing density, [m^2/m^3]
φ_s - volume concentration, [%]
τ - tortuosity, [-]
τ_0 - yield stress, [Pa]

Abbreviations

ASM	Activated sludge models
CAS	Conventional activated sludge
CIA	Cleaning in air
CIP	Cleaning in place
CMC	Carboxymethylcellulose
COP	Cleaning out of place
CP	Concentration polarization
Da	Dalton
DO	Dissolved oxygen
EBPR	Enhanced biological phosphorus removal
EPDM	Ethylene propylene diene Monomer (M-class)
FTIR	Fourier transform infrared spectroscopy
LC-OCD	Liquid chromatography organic carbon detection
MBR	Membrane bioreactor
MF	Microfiltration
MOM	Macromolecular organic matter
MPN	Most probable number
NaOCl	Sodium hypochlorite
NF	Nanofiltration
NTU	Nephelometric turbidity unit
PAC	Powdered activated carbons
PAX XL9	Polyaluminum chloride
PBT	Polybutylene terephthalate
PC	Polycarbonate
PE	Polyethylene
PES	Polyethersulfone
PIX 111	Iron chloride III
PIX 113	Iron sulphate III
PLC	Programmable logic controller
PMMA	Polymethyl acrylate
POM	Polyoxymethylene
PP	Polypropylene
PS	Polysaccharides
PPTV	Polypropylene
PVC	Polyvinylchloride
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
STP	Standard temperature pressure
TMP	Transmembrane pressure
TPU	Thermoplastic polyurethane elastomer
UF	Ultrafiltration
WWTP	Wastewater treatment plant

1. Introduction

1.1. Problem definition

Water is the most precious and vital resource for all known forms of life. Not only the quantity, but also the quality is important by means of human health. They have become the most pressing environmental problem faced humanity in the 21st century. Global water shortage and pollution, caused by population increase, improved living standards, and the expansion of urban areas, have necessitated the search for new or alternative sources of supply.

Over the past decade, membrane technology has become a promising, acknowledged and worldwide implemented separation process that can contribute to solving problems of water scarcity and quality deficiency via the reuse of wastewater and the desalination of seawater and brackish water. Since the conventional activated sludge (CAS) process cannot meet the requirements of wastewater discharge standards becoming stricter and stricter, membrane separation has been considered as an alternative solution.

Membrane technology presents an advanced development of the CAS system for wastewater treatment, where the clarifier is replaced by a filtration step to separate effluent and mixed liquor. In most applications, the membrane modules are submerged directly into the activated sludge tanks to combine the biological step and the solid-liquid separation into a single process commonly referred to as membrane bioreactors (MBRs). There are several successful MBR applications for various types of wastewater streams, such as domestic, municipal, and industrial wastewater.

Compared to CAS systems, MBRs offer considerable advantages, which are discussed below. Further research, however, is still required especially regarding operating and economic efficiency. The possibility of modular construction is favorable as well as the superior effluent quality, since the membrane acts as barrier for suspended matter and bacteria, and most colloidal/soluble compounds. MBRs are especially preferred in cases where stringent water quality requirements have to be guaranteed. Also, the membrane barrier supersedes the secondary clarifier and allows operating at higher biomass concentrations. This new concept reduces tank volumes, thus resulting in significantly smaller foot prints compared to the CAS system, provided, however, that the sludge retention time (SRT) in both systems stays the same.

Since suspended solids could not be measured in the clarification step, with MBR control of the SRT and hydraulic retention time (HRT) is now possible enabling optimum control of the microbial population and flexibility in operation. In addition, due to the omission of the clarifier, slow-growing nitrifying bacteria or species capable of degrading complex compounds can develop and persist in the system even under short SRTs. MBRs eliminate process troubles and problems associated with settling, the latter usually being the most troublesome part of wastewater treatment (*Cicek et al., 2003a*).

One of the main challenges in MBR operation is membrane fouling, causing the flux to decrease and the transmembrane pressure to increase. In the course of filtration, diverse phenomena might occur, causing the reduction of the MBR's filtration capacity. The deposition of solutes and/or particles onto the membrane surface (cake layer formation) or into membrane pores (pore blocking) seems to be the most significant factor responsible for membrane fouling (*Nagaoka et al., 1996; Chang et al., 2002; Drews et al., 2007*). However, due to the complexity of the biomass matrix that is highly heterogeneous and includes living microorganisms, there are still no consistent, substantiated theories on membrane fouling. The nature and extent of fouling in MBRs is strongly influenced by three factors: biomass cha-

racteristics, operating conditions, and membrane characteristics. Membrane fouling in MBR systems can be reversible (i.e. removable by physical cleaning) or irreversible (removable by chemical cleaning only).

Fouling control and prevention result in increased electrical power consumption as well as shut down periods and the need for cleaning chemicals. In order to prevent the formation of unwished fouling layers, there are a number of commonly used physical cleaning methods. These include backwash using a liquid permeate, membrane surface scrubbing, scouring with gas bubbles (crossflow), relaxation breaks, and any combination thereof. In case these methods are not effective in restoring the flux/pressure loss to an acceptable level, chemical membrane cleaning is necessary. However, negative aspects of this method are - amongst others - its high consumption of chemical agents and manpower requirement, thus increasing the operating costs. Commonly, a combination of crossflow aeration and periodical chemical cleaning with acids, bases or oxidizing chemicals are used.

The energy demand of MBRs is higher compared to conventional AS systems, mainly due to the additional energy demand for fouling control. Immersed membranes require about 0.5 to 1.2 kWh/m^3 of permeate for crossflow aeration (*DWA, 2007a*). However, in practice permeability losses have been observed despite regular chemical cleaning (usually weekly). It is well known that contact with chemical agents, during chemical cleaning, contributes to a shorter membrane lifetime and hence affects the operating costs. This leads to losses in productivity and environmental hazards caused by the formation of chemical cleaning by-products, such as organic halogen compounds (AOX). Hence, efficient control and minimization of membrane fouling are required.

In membrane operation, disproportionately long SRTs are often chosen to minimize membrane fouling. Many studies show that membrane fouling occurs earlier and faster in reactors with low SRT, offering more active mixed liquor biomass and higher concentrations of dissolved organic matters. High SRTs lead to higher investment costs due to large volumes of bioreactors and cause significantly higher energy costs (aeration).

Finally, above all remains the need for optimized membrane cleaning procedures and fouling mitigation strategies in order to operate full-scale MBR plants time- and cost-effectively.

1.2. Structure of the thesis

In the framework of this thesis, strategies for sustainable and cost-effective minimization of membrane fouling are investigated. The thesis is organized as follows. For a general understanding of terms, concepts, and problems, *Chapter 2* presents a concise literature review on the state-of-the-art science and technology. A short overview on the general objectives and the approach is given in *Chapter 3*. *Chapter 4* and *5* describe the chemicals, equipment, and methods used in the experimental part of the thesis.

Results and the discussion of experiments are presented in *Chapter 6*. Here, the main focus of the experimental part is on the practical research into permeability loss and fouling reduction. On the one hand, the effect of mechanical and physical cleaning, as well as changes in milieu conditions (aerobic/anaerobic) on the performance of a submerged MBR process were tested. On the other hand, in a parallel experimental set up, the influence of operating conditions and activated sludge characteristics on ultrafiltration membrane fouling was investigated.

Chapter 7 deals with estimating the costs of the proposed methods for fouling minimization. In *Chapter 8*, a general evaluation and final conclusions are given. Finally, *Chapter 9* deals with defining directions for further research work.

2. Fundamentals of membrane separation processes

This chapter covers the basic information on subjects related to membrane filtration. Five topics are dealt with in this part of the thesis. To begin with, a general survey of membrane separation processes with emphasis on micro- and ultrafiltration is given, followed by a description of the characteristics of the membrane bioreactor (MBR) process. In the third part, the limitations of MBR applications are described in detail, followed by a discussion on the modeling of membrane filtration. Finally, an overview of strategies for fouling control/reduction is given.

2.1. Overview of membranes and membrane separation processes

The origin of the word membrane is Latin which means “skin” (*Wenten, 2002*). Today, "membrane" is used to describe thin, flexible, semipermeable layers or sheets, acting as a selective boundary between two phases due to its semipermeable properties.

Membrane filtration is a physical separation process filtering particles or molecules in a variety of sizes from a given media. Small particles, colloids, macromolecules, small molecules, or even ions can be separated depending on the pore size and the material of the chosen membrane. Since membrane filtration is a purely physical process, it does not affect the chemical structure or thermal stability of the membrane materials used. Membranes are part of our life, as all living cells are surrounded by membranes. Biological cell membranes are very selective and transfer only particular substances.

In the 19th century, *Fick (1855)* was the first to prepare and study artificial semipermeable membranes. In the following decades, a lot of research was carried out. However, the fundamental breakthrough in membrane technology was in the late 1950s when Loeb and Sourirajan invented very thin, asymmetric, high-flux membranes from cellulose acetate for reverse osmosis (*Wenten, 2002*). Parallel, Hagen-Poiseuille established a basic law on the flow in pores. Industrial production and application of synthetic membranes based on cellulose began about 1920. The development of polymer membranes started about 1960 (*Staude, 1992*).

2.1.1. Classification of membrane separation processes

Due to the different requirements on mass separation, a multitude of membrane separation processes has been developed. There are several ways to classify membranes, e.g. according to their driving forces, separation mechanism, structure (morphology), and materials.

Some membranes use pressure differences (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis), while others use the driving force of differences in concentration (dialysis) or electric potential (electrodialysis) (see *Table 2-1*). Within the framework of this thesis, only pressure-driven membrane processes are discussed. Information on other membrane separation processes can be taken from the literature (e.g. *Baker, 2004; Melin, 2007*).

The differential pressure between the front and the back of a membrane depends on the mode of application. The transmembrane pressure (TMP) varies from 0.5 bar up to 120 bar and more in exceptional cases (*ATV-DVWK, 2002; Wett, 2005*).

Table 2-1: Classification of membrane filtration processes (modified after *ATV-DVWK, 2002; Wett, 2005*).

Membrane process	Separation mechanism	Driving force
Microfiltration	sieve effect	< 3 bar
Ultrafiltration	sieve effect	< 10 bar
Nanofiltration	solution-diffusion mechanism	< 40 bar
Reverse Osmosis	solution-diffusion mechanism	<120 bar
Electrodialysis	ion exchange, diffusion	electric potential
Dialysis	diffusion of soluble components	concentration gradient

The permeate, also called filtrate, passes through the membrane without hindrance. In contrast, particles, colloids, and molecules, are retained, dependent on their size and molecular weight, and are called concentrate or retentate (see *Figure 2-1*). The mass transfer in and through membranes is based on two different mechanisms: transport through membrane pores (sieve effect) and transport as a result of diffusion (*Mohrdieck, 2009*). These transport mechanisms can occur parallel.

In ultrafiltration (UF) and microfiltration (MF), where pure convective mass transfer through the membrane pores occurs mainly porous membranes are used. This process can be described by Hagen-Poiseuille's law for pipe flow in capillary tubes (see *chapter 2.2*). In reverse osmosis (RO), which uses dense membranes, particle separation is achieved by virtue of differing solubility and diffusion rates of water (solvent) and solute in water (*Judd, 2006*). The difference in the electrochemical potential of the two membrane sides is crucial for diffusive mass transfer of soluble wastewater components, described by Fick's law of diffusion (*Baumgarten, 2007*). Nanofiltration (NF), formerly called "leaky RO", is a liquid separation membrane technology positioned between reverse osmosis and ultrafiltration. With NF, separation is achieved via a combination of charge rejection and solubility diffusion.

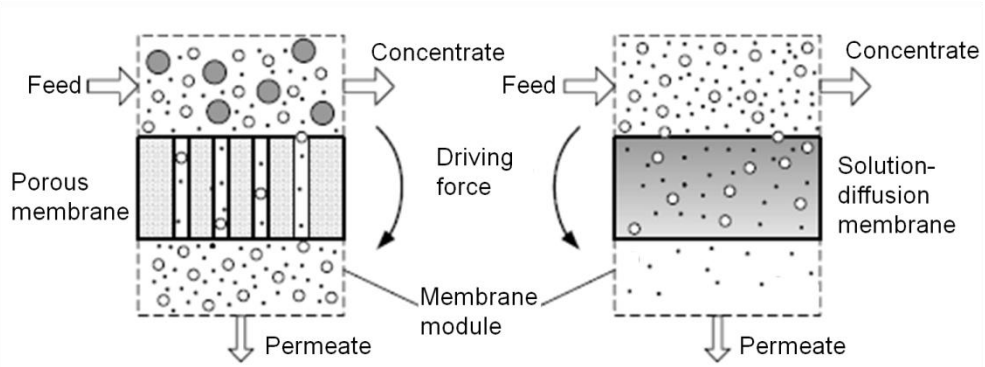


Figure 2-1: Schematic view of membrane separation processes: porous membrane (left), solution-diffusion membrane (right) (modified after *Mohrdieck, 2009*).

The different membrane separation processes can also be classified on the basis of their separation threshold, see *Figure 2-2*. The membrane pore size cut-off, normally in μm, or as molecular weight cut-off (MWCO) in g/mol, i.e. Daltons (Da), refers approximately to the size of particles or the molecular weight of molecules, which can be retained by the respective membrane. Particles or molecules smaller than the pore size pass through the membrane into the permeate.

Typical pore sizes of porous membranes vary between 0.004 μm and 10 μm. Membranes with smaller pore sizes are considered as "dense" and are solution-diffusion membranes (*ATV-DVWK, 2002*). Quan-

tification of a membrane's pore size distribution is a critical factor in assessing whether a membrane has the potential to remove particles, molecules, and/or microorganisms from a feedwater. Microfiltration manufacturers state a "nominal" pore size, i.e. the size above which a specified percentage of particles of a certain nature is rejected under defined conditions (*Jacangelo, 1997*).

The pores of ultra- and microfiltration membranes do not have uniform diameters conditional on manufacturing procedures. The cut-off of retained matter, $< 0.1\ \mu m$ (ultrafiltration), is preferably to be characterized as its molecular weight, corresponding to a 90 % rejection rate for a given membrane, and not as its geometric size. There is no direct correlation between the pore size, in μm, and the molecular weight cut-off, in g/mol, due to varying physical and chemical properties of solute molecules of identical MWCO. However, *Staude (1992)*, for example, estimates that membranes with a pore size cut-off of 0.1 μm retain molecules with MWCO of more than 500.000 g/mol.

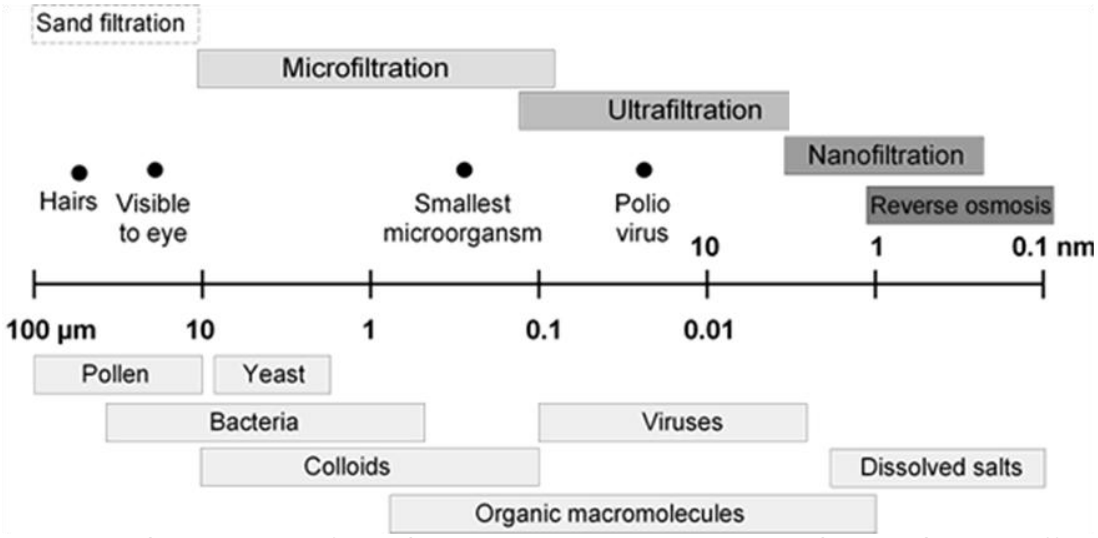


Figure 2-2: Characteristics of membrane separation processes according to their cut-off size (modified after *Günder, 1999*).

2.1.2. Membranes – materials and morphology

2.1.2.1. Membrane materials

Membranes can also be classified according to their material, the main materials being polymeric, ceramic, and metallic. Thereby, metallic membranes have very specific applications, not used in membrane bioreactor (MBR) technology (see *chapter 2.3*). According to *Staude (1992)* the selection of the most applicable material requires to consider many criteria, such as:

- resistance against temperature, pressure, and cleaning agents
- hydrophobicity/hydrophilicity
- mechanical strength
- availability and price

In (waste)water treatment, most commonly polymeric membranes are applied, providing a wide variety of materials, pore sizes, pore size distributions, configurations, and production processes. The main reason to apply organic membranes is the manufacturing costs for ceramic membranes which are about 10 times higher than for organic membranes (*Evenblij, 2006*). Notwithstanding the large variety

of polymeric materials, only a limited number of materials is suitable for application in membrane separation, e.g. polyvinylidene fluoride (PVDF), polyethersulfone (PES), polyethylene (PE), polypropylene (PP) (*Judd, 2006*).

2.1.2.2. Membrane morphology

Depending on the characteristics of the material and the manufacturing process, there are isotropic (symmetric) and anisotropic (asymmetric) membranes. Symmetric membranes have a porous structure with a pore size distribution characterized by an average pore size that is relatively constant throughout the membrane layer.

In asymmetric (anisotropic) membranes, consisting of several layers, each with different structures and permeability (*Baker, 2000*), the average pore size varies within the membrane body, thereby usually increasing from one surface to the other (*Rautenbach, 1997*). Asymmetric membranes provide higher fluxes compared to symmetric membranes of the same rated pore size and thickness. Some asymmetric membranes have a distinct transition between the dense filtration layer, i.e. the skin, and the support structure. The denser skin layer is exposed to the feedwater and acts as primary filtration barrier, while the thicker and more porous substructure primarily serves as mechanical support (*USEPA, 2005*).

2.1.2.3. Membrane modules

Membrane modules are composed of several membrane elements. Membranes are encased in modules to increase their stability. The membrane's geometry and the way it is mounted and oriented in relation to the water flow is crucial for the overall process performance. Moreover, the integration of the membranes into a module is to provide for optimal flow conduction (turbulence promotion), high packing density, easy cleaning of facilities, easy module exchange, and permit modularization. Depending on the manufacturing process, membrane modules consist of flat sheets, hollow fibers/capillary and/or tubes (*Günder, 1999*). *Table 2-2* shows a list of membrane modules by different manufacturers without claiming completeness.

Table 2-2: Membrane modules and manufacturers (modified after *Rosenberger, 2003*).

Membrane Bioreactor (MBR)				
Submerged			**Sidestream**	
Flat sheets (e.g. Huber, Kubota, Martin Systems, Max-Flow, Microdyn-Nadir, Pall)	Hollow fibers (e.g. Inge, Memcor, Mitsubishi, Puron, Weise Water Systems, Zenon)	Tubes (e.g. Berghof, Koch, Microdyn-Nadir, MilleniumPore)	Pillow-shaped (e.g. Rochem)	Tubes (e.g. Berghof, Techsep, X-Flow..)

In the frame of this thesis, the focus was on submerged flat sheet modules and experiments were carried out only for this type of module. Plate (i.e. frame) modules, consist of (multiple) flat sheet membranes arranged parallel and built onto a supporting device with permeate tube (manifold). The suspension flow towards the membranes and thus the filtration is from outside to inside. In *Figure 2-3*, a flat sheet module (Bio-Cel®) of Microdyn-Nadir is exemplified.

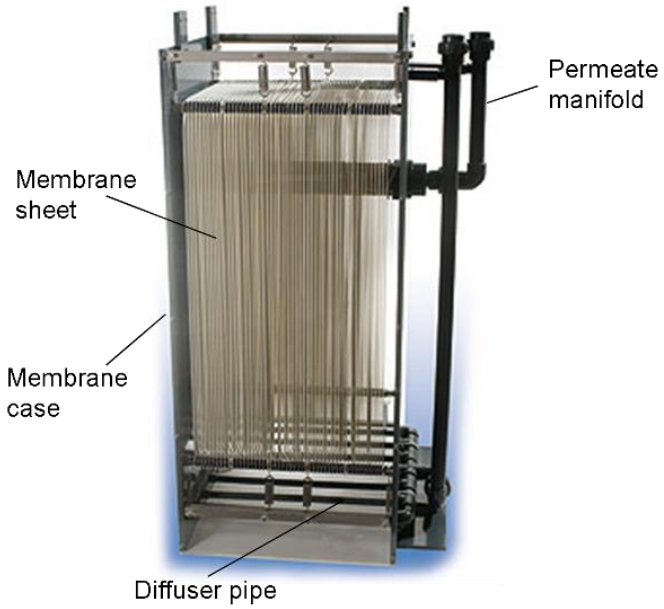


Figure 2-3: Microdyn-Nadir (Bio-Cel®) flat sheet membrane module (*Microdyn-Nadir*).

The Bio-Cel® module combines the advantages of plate/frame (the defined channels) and hollow fiber (the packing density, the possibility of backwash) modules. On the one hand, the backflushability of a membrane pocket is reached by a laminated construction of the membrane support material to the spacer material that is only 2 mm thick. On the other hand, an extremely high packing density is achieved with very low weight, as is normally possible only when using hollow fibers. The flat sheet membrane is made of polyethersulfone (PES) material with a MWCO of 150 kDa, corresponding to a pore diameter of approximately 0.04 μm (Microdyn-Nadir).

The fine-bubble air "crossflow system" (see chapter 2.6) has to fulfill three functions; to provide an adequate oxygen supply for biological treatment, to scour the membrane surface and thus prevent fouling, and to create a specific density gradient between the inside and the outside of the submerged membrane unit, thus producing biomass circulation.

2.2. Micro- and ultrafiltration process – basic principles and definitions

2.2.1. Mass transfer

Mass transport through unfouled porous membranes can be described by Darcy's law, which states that flux is proportional to applied pressure difference (*Peinemann and Nunes, 2010*).

$$J_p = P_p \cdot \Delta p \ \ [\mathrm{L/(m^2 \cdot h)}] \qquad (2.1)$$

with:
J_p - volumetric flux, [L/(m^2·h), m/s]
P_p - permeability constant, [m/(Pa·s)]
Δp - transmembrane pressure (TMP), [bar]

The permeability constant (P_p) is a function of membrane structure, including pore size distribution and porosity of the membrane as well as permeate viscosity. Two approaches describe the constant P_p.

The Carman-Kozeny pore model assumes a pore system formed of equally sized spheres in a packed bed (modified after *Peinemann and Nunes, 2010*). In this model, the blocking of membrane pores is not considered.

$$J_p = P_p \cdot \Delta p = \frac{\varepsilon^3}{\eta \cdot S^2 \cdot (1-\varepsilon)^2 \cdot K \cdot \tau \cdot \delta_p} \cdot \Delta p \ \ [\mathrm{L/(m^2 \cdot h)}] \tag{2.2}$$

with:
ε - porosity (or voidage), [-]
η - dynamic viscosity of the permeate, [Pa·s]
S - specific area (surface area per unit volume), [m^2/m^3]
τ - tortuosity, [-]
δ_p - thickness of the porous layer, [m]
K - constant equal to 2 for perfectly cylindrical pores, [-]

However, in case the structure of the membrane is assumed to be uniform capillaries, the flow rate of the permeate is given by Hagen–Poiseuille's law (*Peinemann and Nunes, 2010*).

$$J_p = P_p \cdot \Delta p = \frac{\varepsilon \cdot d_{pore}^2}{32 \cdot \eta \cdot \tau \cdot l_c} \cdot \Delta p \ \ [\mathrm{L/(m^2 \cdot h)}] \tag{2.3}$$

with:
ε - porosity (or voidage), [-]
η - dynamic viscosity of the permeate, [Pa·s]
τ - tortuosity of the capillaries, [-]
d_{pore} - diameter of the capillaries, [m]
l_c - length of the capillaries, [m]

2.2.2. Fundamental parameters: pressure, flux, permeability, and retention rate

Figure 2-4 presents the key parameters for the operation of pressure-driven membrane separation processes. Mass transfer through the membrane is selective and is summarized in the term permeation.

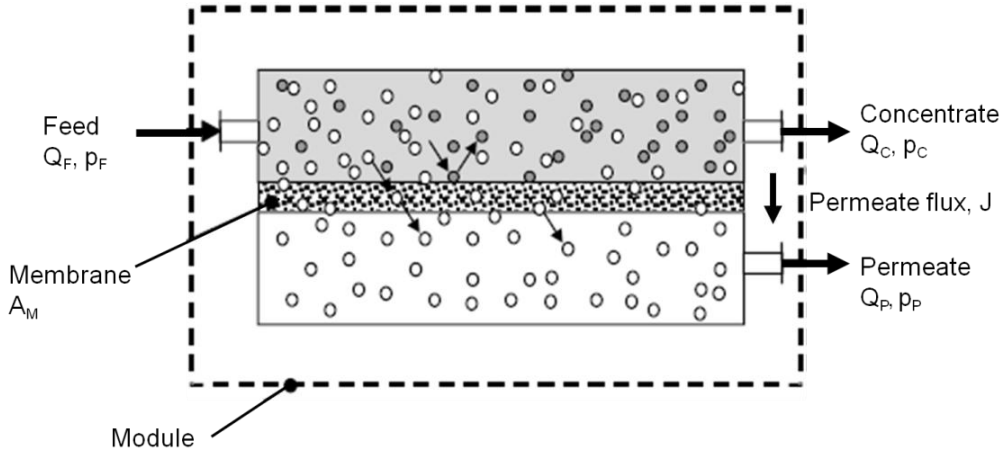


Figure 2-4: Terminology of micro- and ultrafiltration separation process (A_M- membrane surface, Q- volume flow rate, p- pressure) (*Melin and Rautenbach, 2007*).

In micro- and ultrafiltration processes, the driving force for membrane permeation is the TMP. Generally, TMP is calculated as the pressure difference between the outside (p_F, p_C) and the inside (p_P) of the membrane.

$$TMP = \Delta p = \frac{p_F + p_C}{2} - p_P \text{ [bar]} \tag{2.4}$$

The permeate flux rate (J) is the standard parameter to describe the hydraulic capacity of a membrane system. The flux is described as the quantity of "material", which passes through a unit area of membrane per unit time. The commonly used (non SI) unit is liter per m^2 per hour. The flux relates directly to the driving force (TMP) and the total hydraulic resistance (see *chapter 2.4.2*) offered by the membrane and its active surface (*Judd, 2006*).

$$J = \frac{Q}{A_M} \text{ [L/(m}^2\text{·h)]} \tag{2.5}$$

The quotient of flux (J) and driving force (TMP) describes the permeability (L_P) of the membrane.

$$L_P = \frac{J}{\Delta p} \text{ [L/(m}^2\text{·h·bar)]} \tag{2.6}$$

During membrane operation, periodic filtration breaks (called relaxation breaks) and backwash with permeate and/or membrane cleaning might be necessary (see *chapter 2.6*). In this case, one has to distinguish between net flux rate and gross flux rate of the membrane process. The net flux rate is thereby defined as the gross flux rate adjusted for production lost during backwash, relaxation, and cleaning.

The membrane rejection rate for a defined component "i" specifies to which extent this component will be retained by the membrane.

$$R = 1 - \frac{c_{i,P}}{c_{i,F}} \ [\%] \tag{2.7}$$

with:
R - rejection rate [%]
$c_{i,P}$ - concentration of component i in permeate [mg/L, mol/L]
$c_{i,F}$ - concentration of component i in feed [mg/L, mol/L]

2.3. Membrane Bioreactor (MBR) process

The application of membrane separation techniques (micro- or ultrafiltration) for biosolid separation can overcome the disadvantages of sedimentation tanks and biological treatment steps (*Visvanathan et al., 2000*). Membranes offer a complete barrier against suspended solids as well as colloidal material and yield a higher effluent quality, i.e. free of bacteria and pathogens.

In recent years, the focus has shifted towards the concept of combining the activated sludge process with membrane filtration, the new system being called membrane bioreactor (MBR). There are several advantages associated with the MBR that makes it a valuable alternative compared to other treatment techniques. Since suspended solids are not lost in the clarification step, total separation as well as control of the SRT and HRT are possible, thus enabling optimum control of the microbial population and flexibility in operation. The absence of a clarifier, which also acts as a natural selector for settling organisms, enables sensitive, slow-growing species (nitrifying bacteria, bacteria capable of degrading complex compounds) to develop and persist in the system even under short SRTs (*Cicek et al., 2003a*). In addition, the biomass is concentrated, thus reducing the necessary bioreactor size and increasing the efficiency of the biotreatment process (*Judd, 2006*).

The MBR technology has great potential in wide ranging applications including municipal, domestic and industrial wastewater treatment, groundwater and drinking water purification (*Jefferson et al., 2000; Rosenberger et al., 2002; Panglisch et al., 2005*).

The technical feasibility of this process has already been demonstrated via a number of pilot- and bench-scale research studies. Full-scale systems are operated in various parts of the world and substantial growth in the number and size of installations is anticipated for the near future (*Gander et al., 2000; Jarusutthirak et al., 2001; Cicek 2003a*). At the same time, the use of small-scale MBRs in decentralized applications is likely to be a major thrust. Optimized designs and sustainable operation are in demand. Therefore, improved comprehension of ways to alleviate membrane fouling is one of the main keys to the future of this technology (*Fane et al., 2005a*).

2.3.1. Functional principle and configuration

2.3.1.1. Functional principle

In wastewater treatment using the MBR process, the mechanically pretreated raw wastewater first undergoes biological treatment in an activated sludge system. In the bioreactor, the wastewater is mixed and aerated, thus improving the microbial metabolization of suspended and soluble organic matter. The organic matter is decomposed and converted into cells and/or oxidized to CO_2 and water. Sufficient oxygen supply provided by an aeration system and mixing are crucial for successful treat-

ment. In the following step, the treated wastewater is separated from the activated sludge via membrane filtration. The new cells (biomass), called excess sludge, are thereby removed from the system.

2.3.1.2. MBR configuration

MBR configuration and operation strongly depend on the required effluent quality, application, and module type. According to the chosen configuration, these basic requirements can be achieved in different ways. The membranes can be either submerged directly into the bioreactor or be placed in the external circuit of the bioreactor (sidestream), depending on the used module type (see *Figure 2-5*) (*Visvanathan et al., 2000*).

In the sidestream configuration, the membrane module is not part of the main bioreactor. The activated sludge is pumped from the bioreactor into an externally placed membrane module. Here a permeate stream is generated and the biomass retained by the membrane is returned into the bioreactor. The driving force is the pressure created by high crossflow velocity along the membrane surface (*Cicek et al., 1998*). The membranes generally have a high flux and are of low maintenance. The crossflow aeration system is generated by a pump that, at the same time, can create the TMP for the membrane process. The oxygen supply for the activated sludge and the mixing of the aeration tank is assured by a separate aeration system.

The submerged configuration provides two possibilities. On the one hand, the filtration elements are submerged directly into the bioreactor, on the other hand it is placed into a separate filtration chamber (*Cornel et al., 2001*). The latter solution offers some advantages, as it facilitates the modular upgrade of the plant as well as module maintenance and cleaning works. The driving force across the membrane is achieved by pressurizing the bioreactor or creating a vacuum on the permeate side (*Rosenberger et al., 2002*). However, in some circumstances, the permeate side is placed in a lower position, and the gravity itself is the only driving force for filtration (*Jiang, 2007*). Because the membrane modules are submerged directly in the main bioreactor, recirculation of concentrated sludge is avoided.

The crossflow is generated by the uplifting flow of coarse or fine bubbling air. For this purpose, a suitable fan with an air supply diffuser, usually placed directly beneath the membrane module to facilitate scouring of the filtration surface, is necessary. Normally, the crossflow system provides sufficient energy for mixing the activated sludge tank as well as oxygen for the biological treatment process. Otherwise a separate aeration system has to be installed.

According to *Judd (2006)* sidestream MBRs are generally more energy-intensive than submerged MBRs, due to high pressures and volumetric flows. Moreover, the configuration of submerged MBRs is simpler, as it needs less equipment and the crossflow aeration system in the membrane tank can be multifunctional, as described above. Other advantages are the high packing density and low costs of capillary and hollow fiber membranes used in many submerged MBRs. This makes it feasible to install more membrane modules and operate them at lower fluxes. Submerged modules are commonly used in municipal wastewater treatment. However, sidestream MBRs are more robust and more flexible in the control of the crossflow velocity (*Jiang, 2007*). Nowadays, sidestream modules are mostly implemented in industrial applications, in particular where small membrane surfaces are needed or persistent wastewater is treated.

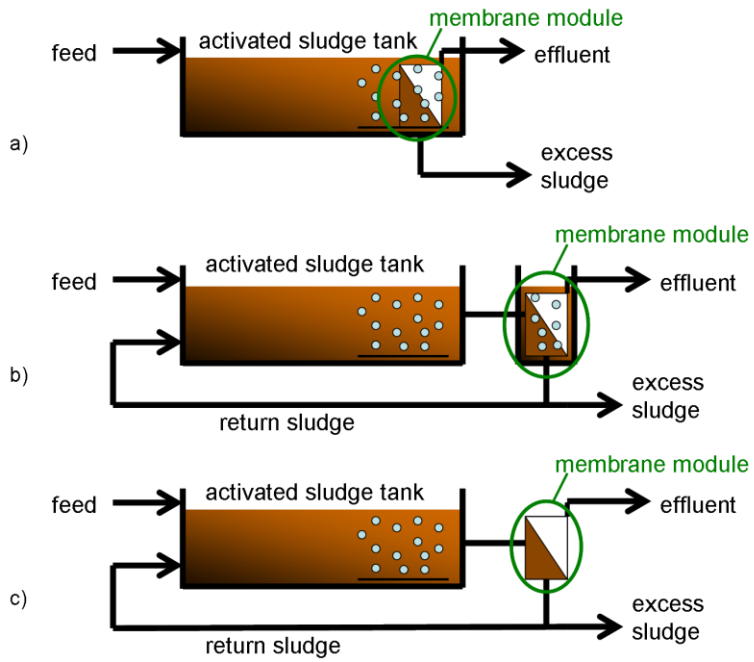


Figure 2-5: Configuration of different MBR processes: submerged (a, b), sidestream (c).

2.3.2. Operating method – dead-end and crossflow filtration

Basically, conventional pressure-driven membrane processes with liquid permeation can be operated in two modes: dead-end and crossflow (*Judd, 2006*).

In membrane separation systems operating in dead-end or in-line mode there is no concentrate stream, but only one influent (i.e. feed) and one effluent (i.e. permeate) stream, as shown in *Figure 2-6(a)*. In dead-end mode, the entire fluid flow, with all solute, suspended and dissolved components, is transported perpendicularly towards the membrane and forced through the membrane by pressure of the permeate flux. As the retained material accumulates on the membrane surface or in its interior and is held in place as a result of hydraulic forces acting perpendicular to the membrane surface, a cake layer forms. Due to this formation, the pressure to maintain the required flow increases, until at some point the membrane has to be backwashed or replaced (*Baker, 2004; USEPA, 2005; Evenblij, 2006*).

In membrane filtration systems being operated in crossflow mode, the feed solution is circulated across the surface of the membrane, producing two streams: permeate and concentrate, the latter containing the retained material (*Baker, 2004*). A scouring force, using water and/or air, is applied parallel (i.e. tangential) to the membrane surface during the filtration process in a continuous or intermittent manner (see *Figure 2-6(b)*). Membrane operation in crossflow mode reduces fouling processes (as further discussed in *chapter 2.6*) by minimizing the accumulation of solids/contaminants on the membrane surface or in the boundary layer (*USEPA, 2005*). Compared to the dead-end mode, the equipment required for crossflow filtration is more complex and the energy demand is higher, due to the required pump capacities and the feed-side pressure loss during membrane overflow. However, membrane lifetime is longer.

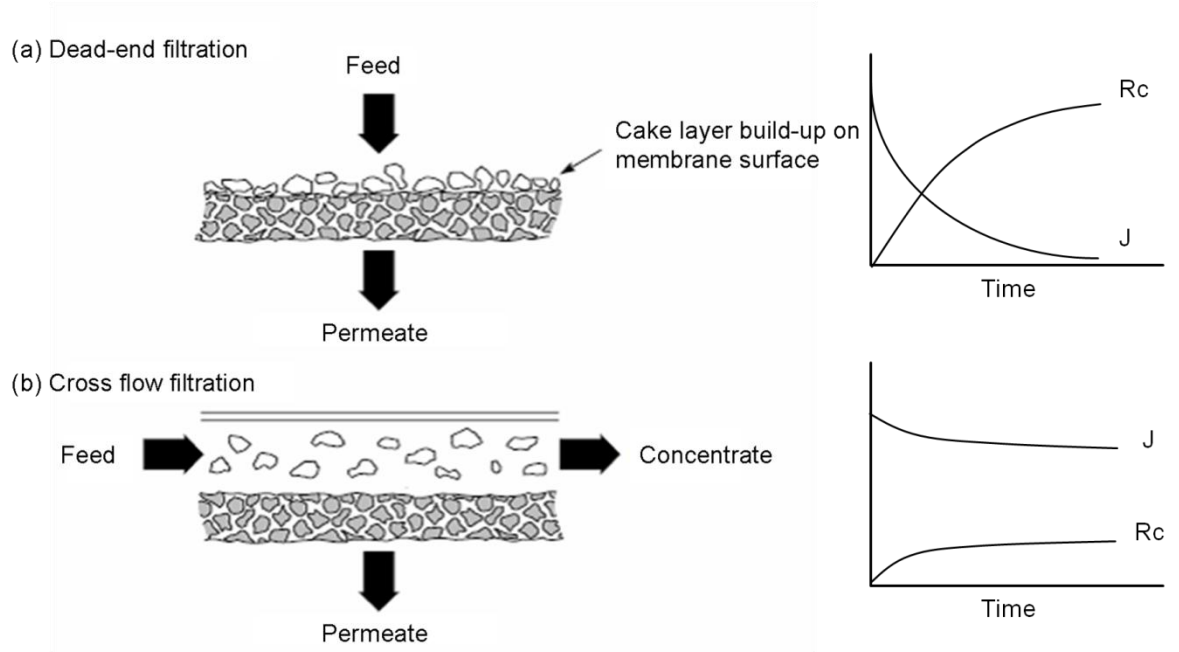


Figure 2-6: Schematic presentation of (a) dead-end and (b) crossflow filtration: Rc- cake resistance, J- flux rate (modified after *Baker, 2004*).

2.3.3. MBR design and process efficiency

2.3.3.1. MBR design

Enhanced mechanical pre-treatment of the raw wastewater appears to be one of the most critical factors for assuring a stable and continuous operation of MBR plants. Removal of hair, fibrous material and other contraries that can lead to operational problems of the membrane modules is of particular importance (*Melin et al., 2006; Schier et al., 2009*). Sieves with perforated panels of 1 mm mesh size provide the optimal level of protection (*Schier, 2003*).

For the MBR's optimal functioning, the following basic requirements must be met (*Günder, 1999*):

- adequate oxygen supply for the activated sludge
- agitation and mixing of an aeration tank
- transmembrane pressure difference for the filtration process
- crossflow aeration system for membrane fouling control (see *chapter 2.6*)

Generally, for dimensioning a MBR plant, the same procedure as for conventional wastewater treatment plants can be applied (*ATV-DVWK, 2000a and b*). To dimension the biological reactor, information on the influent flow and the nutrient load are needed. Additional attention must be paid to flow characteristics due to the impact of temperature on membrane performance (see *chapter 2.4.2*).

For evaluating the required membrane area, the supplier has to indicate the specific dimensioning parameters (particularly flux) guaranteed under specific local conditions. The main parameter required for dimensioning the membrane chamber is the specific packing density (φ) of the membrane area per unit of reactor volume.

For evaluating the pollutant removal capability of the plant, the volume of all reactors needs to be considered. The crucial parameters for dimensioning the biological reactor are the volumetric loading

rate (VLR) and sludge loading rate (SLR). VLR depends on the influent concentration and the HRT. Nowadays, MBR plants are operated at VLRs between 1.2 and 3.2 kg COD/(m^3·d) and SLRs between 0.02 and 0.4 kg COD/(kg TSS·d) (*Rosenberger, 2003*).

$$VLR_{COD} = \frac{COD_{\inf} \cdot Q}{V} \text{ resp. } VLR_{BOD5} = \frac{BOD_{5,\inf} \cdot Q}{V} \text{ [kg/(m}^3\text{·d)]} \quad (2.8)$$

$$SLR_{COD} = \frac{COD_{\inf} \cdot Q}{X \cdot V} \text{ resp. } SLR_{BOD5} = \frac{BOD_{5,\inf} \cdot Q}{X \cdot V} \text{ [kg/(kg TSS·d]} \quad (2.9)$$

with:
COD_{inf} - influent COD concentration, [mg/L]
$BOD_{5,inf}$ - influent BOD_5 concentration, [mg/L]
Q - flow rate, [m^3/d]
V - reactor volume, [m^3]
X - biomass concentration, [g/L]

The biological compartment of the reactor may also be dimensioned on the basis of the required sludge age, called sludge retention time (SRT), at the minimum temperature. In this case, the reactor volume is calculated as a function of the daily sludge production ($P_{x,d}$) and concentration, while the HRT is not an input variable in this calculation (*Wedi et al., 2008*). Sludge age describes the period of time during which activated sludge remains in the system.

$$SRT = \frac{V \cdot X}{(Q - Q_W) \cdot X_e + Q_w \cdot X_R} \text{ [d]} \quad (2.10)$$

with:
V - reactor volume, [m^3]
Q - flow rate, [m^3/d]
Q_w - waste sludge flow rate, [m^3/d]
X - biomass concentration, [g/L]
X_e - concentration of biomass in effluent, [g/L]
X_R - concentration of biomass in return flow, [g/L]

For municipal wastewater, literature data on conventional treatment can also be used for MBRs (*ATV-DVWK, 2000a*). In activated sludge plants treating municipal wastewaters, typical sludge ages are in the range of 5 to 15 d for COD and nitrogen elimination (*Stephenson et al., 2000*). With MBRs, the retention time of the sludge is unaffected by sedimentation behavior and very high sludge ages can be reached. Most membrane bioreactors (particularly in Germany and Switzerland) are currently operated at a sludge age of > 25 days (sludge stabilization) (*Wedi et al., 2008*). The first full-scale MBR plant in Germany (Markranstädt) was operated at an average sludge age of 49 d (*Kubin, 2004*).

Frequently, MBRs are operated at significantly higher SRTs than needed. This leads to unnecessary energy consumption. As a general rule, reducing the SRT pays off despite higher sludge production and related disposal costs, due to the energy savings (*MUFV, 2007*).

The lower limit of the sludge age (8 d) results from guaranteeing biological nitrification. At plants operated with the nitrification and denitrification process, the sludge age depends on the ratio of denitrification to nitrification reactor volume. The layout of the biological reactors depends on the nutrient removal capacity of the plant (e.g. denitrification and/or biological phosphorus removal).

The sludge concentration in the various compartments depends on the concentration range given for the membrane chamber X_{MC} (the latter being up to 15 g/L) and the flow in the sludge recycles. Since membranes allow much higher sludge concentrations than CAS plants (up to 5 g/L), MBRs need significantly smaller reactor volumes (*Wedi et al., 2008*), provided, however, that the SRT in both systems stays the same.

2.3.3.2. Efficiency of the MBR process

The retention efficiency of the MBR separation process is not affected by gas bubbles, floating sludge or bulky flocs with lower density, as occurring in conventional wastewater treatment plants (WWTP) (*Wiesmann et al., 2006*). The MWCO of microfiltration and ultrafiltration membranes is determined by sieve effects between membrane pores and filtered components. During the MBR operation, the material being rejected by the membrane accumulates in the interfacial area of the membrane and leads to the formation of a gel layer (see *chapter 2.4*). This gel layer may then have a greater selectivity than the membrane itself and can result e.g. in a MF process displaying the characteristics of UF membranes (*Al-Malack et al., 1997; Huang et al., 2000*). In such cases, the gel layer is sometimes referred to as dynamic membrane (*Stephenson et al., 2000*).

The performance of municipal MBRs has already been proven at many pilot and full-scale plants in Germany, e.g. Rödingen (Erftverband), Markranstädt (Leipzig), and Büchel (Aggerverband) (*Engelhardt et al., 2000; Stein et al., 2001; Wozniak et al., 2001*). The effluent quality of full-scale MBR plants was tested for hygienic parameters and an extensive disinfection was observed (*Stein, 2003; Engelhardt, 2003; Dorgeloh, 2004*). *Fane (1996)* reports that microfiltration (MF) and ultrafiltration (UF) membranes typically provide log 2 to log 5 virus removal respectively, whereas the removal of protozoa can be assumed to be log 5 (*Trussell et al., 2003*).

Although loading rates are mostly similar, the removal efficiency of organic matter (COD) is higher for MBRs (90-98 %) than for CASs (75-85 %) (*Stephenson et al., 2000*). According to *Côté et al. (1998)*, the improved COD removal can be attributed to the combination of complete particulate retention by the membrane and the avoidance of biomass washout problems which are common in CASs. In particular, the latter enables stable conditions for slow growing microorganisms that are able to remove persistent components, favored by higher SRTs.

However, arbitrary high MLSS concentrations cannot employed, since it is believed that oxygen transfer is limited due to higher and non-Newtonian viscosities (*Rosenberger et al., 2001*), affecting membrane performance (see *chapter 2.4.3*).

The relative oxygen transfer ratio α (the ratio of the aeration coefficient k_La, apparent volumetric mass transfer coefficient, under process conditions to the k_La-value in clean water) for different WWTPs under operational conditions is found to be in the range of 0.2 to 0.8 for MLSS in the range of 1-18 g/L (*Cornel et al., 2001; Drews et al., 2005*). However, the results of *Henkel et al. (2009)* reveal that at high SRT the α-factor is mainly influenced by the mixed liquor volatile suspended solids (MLVSS) concentration. For a typical municipal MBR with a MLSS of 12 g/L and a loss on ignition of

70 %, the α-value can be assumed to be in the range of 0.5 ± 0.1. Another study of *Henkel et al. (2009)* shows that the α-factor was reduced when the free water content decreased and the floc volume increased. Since the floc volume is mainly regulated by the MLVSS concentration in activated sludge, a reduction in the oxygen transfer with increasing MLVSS concentration was observed. With unchanging floc volumes, oxygen transfer increases with increasing SRT.

Similar to the conventional process, with MBR systems, aerobic-anoxic operating conditions are necessary to achieve nitrogen removal. In municipal wastewater, nitrogen is mostly present in the form of ammonium. In aerated units, ammonium is converted to nitrate and in the subsequent non-aerated, anoxic step, nitrate is converted to elementary nitrogen. Since microorganisms need nitrogen for growth, of course nitrogen is also removed together with the excess sludge. MBRs offer good nitrification conditions because of the high retention of sludge allowed. Therefore, even slow-growing nitrifying bacteria have an excellent chance to establish themselves in the aeration tank. Hence, nitrogen removal with preliminary denitrification and with post-denitrification is realized with MBRs (*Wiesemann et al., 2006*).

Reactor concepts such as post-denitrification and enhanced biological phosphorus removal (EBPR) in MBRs are further options. Owing to MBR characteristics, such as generally high aeration requirements and high sludge ages, post-denitrification is a configuration particularly interesting for MBRs. Post-denitrification was shown to be possible even without an external source which can be attributed to the buildup of storage compounds such as glycogen (*Lesjean et al., 2003; Gnirs et al., 2003; Vocks et al., 2005*). Phosphorus removal can occur either via chemical precipitation or enhanced biological elimination. The possibility of biological phosphorus elimination opens up further MBR applications, as in principle has been proved, for example, by *Adam et al. (2001)* for the EBPR process. Further investigation showed that in both CAS process and MBR-EBPR setups specific P-uptake rates were found to be comparable, however, there is need for further study on the determination and optimization of the maximum sludge age that can still achieve efficient Bio-P removal. Additional precipitation might be necessary in areas with sensitive receiving water bodies (*Kraume et al., 2005*). Chemical phosphorus removal is achieved by generating hardly soluble and thus precipitating iron, aluminum or calcium phosphates. These salts are withdrawn together with the excess sludge. The necessary precipitants can be dosed at different points of the reactor.

Enhanced research over the past years into the development of new membranes and modules resulted in reduced capital and operating costs of MBR plants. Thus, the implementation of MBRs in municipal wastewater treatment is more and more frequent (*Kubin, 2004*).

2.4. Limitations of MBR applications

2.4.1. Process description

One of the main challenges of MBR application is membrane fouling, causing a decrease in permeate flux and an increase in the TMP. It is a well-known and costly problem of membrane filtration and its control and prevention result in high manpower requirements as well as increased power consumption, and the need for cleaning chemicals (*Schier, 2003*) (see *chapter 2.6*). Membrane fouling in MBRs is attributed to physicochemical interactions between the components in the activated sludge liquor and the membrane material, arising in the course of the filtration process (*Chang et al., 2002*).

Membrane fouling in membrane bioreactors may be classified according to the nature of foulants: particulate fouling caused by colloids and suspended solids, inorganic fouling (scaling) caused by salt precipitation, organic fouling caused by adsorption of organic matter and biological fouling (biofouling) caused by deposition or growth of microorganisms (*Gorenflo, 2003; Judd, 2004; Jiang, 2007*). However, the borders between these classes are blurred. Mainly, organic fouling, biofouling, and colloid fouling can occur simultaneously and form hybrid fouling, which can be more difficult to remove (*Baumgarten, 2007; Jiang, 2007*).

Another distinction is made by the subdivision into reversible and irreversible as well as initial and long-term fouling (*Al-Halbouni, 2008*). According to *Chang et al. (2002)*, reversible fouling occurs at the membrane surface as a result of cake layer buildup and can be removed by physical washing (e.g. through backwashing and relaxation phases between active filtration phases). On the contrary, irreversible fouling is caused by the adsorption of dissolved matter within the membrane pores and can generally be removed only by chemical cleaning (*Le Clech et al., 2003*). However, restricting categorization of membrane fouling to reversible or irreversible is somewhat simplistic. For example, gel layer formation on a membrane surface is most often irreversible although notionally it is reversible since it forms a cake layer. Some kinds of fouling by pore blocking and adsorption may be partially reversible depending on the strength of adhesion and the vigor of the physical wash (*Chang et al., 2002*) (see *chapter 2.5*).

The accumulation of different components on the membrane surface (cake layer formation), sometimes in connection with biofilm formation and even in-depth adsorption of substances within the membrane pores results in a substantial loss of membrane permeability. Substances that cause any of the different cases of membrane fouling, are generally called **foulants** (see *chapter 2.4.3*) (*Al-Halbouni, 2008*).

2.4.2. Fouling rate

The extent of fouling, as a progressing phenomenon, i.e., the fouling rate, can be quantified either in terms of the derivative of the filtration resistance (*Drews et al., 2008*) or the permeability drop (see *equation 2.6*) over time. In this thesis, fouling potentials and actual membrane conditions are evaluated by solely using the permeability trend.

Darcy's low is commonly used to determine filtration resistance in permeate transport through porous membrane (see *chapter 2.5.2*):

$$R_t = \frac{\Delta p}{\eta(T) \cdot J} \text{ [1/m]} \tag{2.11}$$

with:
R_t - total filtration resistance, [1/m]
Δp - transmembrane pressure, [bar]
J - permeate flux rate, [L/(m^2·h)]
$\eta(T)$ - permeate dynamic viscosity, [Pa·s], with T in [°C]

In the presence of foulants, the total filtration resistance (R_t) is the sum of clean membrane resistance (R_m), concentration polarization resistance (R_{cp}), and fouling resistance (R_f), the latter including processes such as adsorption, pore blocking, and gel/cake layer formation (see *chapter 2.5.2*).

Since temperature affects membrane filtration via changing permeate viscosities (*Mulder, 2000*), it is necessary to compensate the temperature dependency to be able to compare hydraulic performance over a long-term operation period. In this thesis, temperature correction to 20 °C (see *equation 2.12*), similar to the k_La (mass transfer coefficient), was used (*Judd, 2006*).

$$J_{20} = J_T \cdot 1.024^{(20-T)} \ [\mathrm{L/(m^2 \cdot h)}] \tag{2.12}$$

with:
J_T - flux at process temperature T in °C

2.4.3. Fouling mechanisms

The reduction in membrane flux (or increase in TMP) occurs as a consequence of diverse mechanisms (see *Figure 2-7*) and can be classified into two groups. On the one hand, the accumulation of the solute in a mass transfer boundary layer near the membrane surface is larger than the concentration of the bulk solution, i.e. **concentration polarization** (see *chapter 2.5.1*). This accumulation reduces the solvent flow through the membrane. This phenomenon in inevitable, however it is reversible by reducing the TMP and hence the membrane flux (*Peinemann and Nunes, 2010*). Concentration polarization promotes membrane fouling such as the formation of a cake layer.

On the other hand, there are fouling mechanisms that are categorized as pore adsorption, pore blocking, and cake formation. Pore adsorption and blocking are internal membrane fouling mechanisms, whereas cake formation occurs on the membrane surface, i.e. external fouling (*AWWA, 2005*).

Pore adsorption, occurs with specific interaction between membrane and particles (colloids) or solutes. Particles or solutes are deposited on the pore walls along their entire length, thereby changing the overall pore volume by decreasing the pore diameter. The change in pore volume is proportional to the permeate volume. Thus, the hydraulic resistance increases as a result of pore constriction.

Pore blocking occurs during filtration, leading to a reduction in flux due to the blockage of individual pores. Thereby, the total number of pores is reduced, while there is no effect on pore diameter. The change in pore volume is proportional to the permeate volume, as with pore adsorption.

Cake formation occurs with suspensions consisting particles too large to block just individual pores. The increase in cake formation on the membrane surface is proportional to the permeate volume and leads to significant additional hydraulic resistance (*AWWA, 2005*). *Peinemann and Nunes (2010)* define **gel deposition** as another fouling mechanism. Gel deposition occurs with certain macromolecules, for example solutions of concentrated proteins. Their level of concentration polarization may lead to gel formation in the immediate vicinity of the membrane surface.

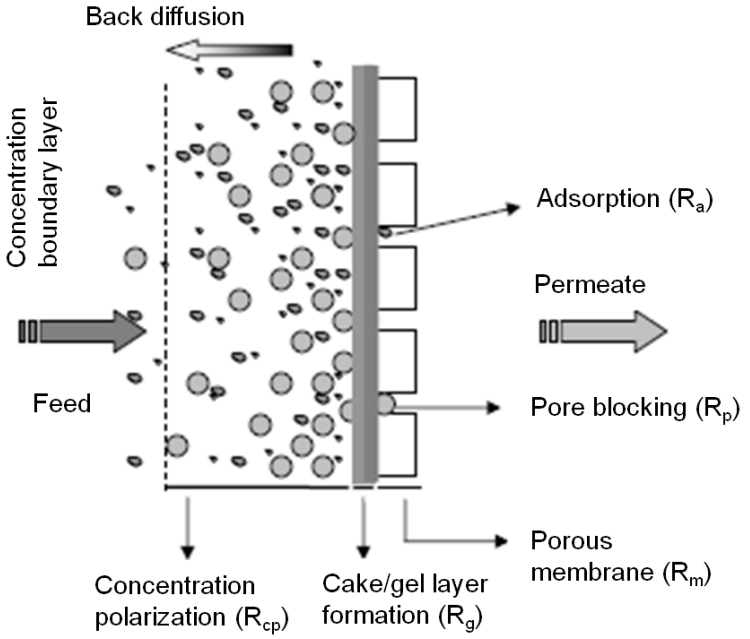


Figure 2-7: Fouling mechanisms in membrane filtration (modified after *Roorda, 2004*).

2.4.4. Overview of factors influencing fouling in MBR

The degree of fouling in any membrane process is determined by three key factors, most of which are interrelated, i.e. membrane properties, operating conditions, including system hydrodynamics, and biomass characteristics (*Judd, 2004*), as described below.

2.4.4.1. Membrane properties

It is well known that membrane characteristics, such as pore size, porosity, roughness, hydrophilicity, etc., play a significant role in membrane fouling processes (*Chang et al., 2002; Judd, 2004*). Effects of **pore size** on membrane fouling strongly depend on the feed solution characteristics, in particular, particle size distribution (*Chang et al., 2002*). Particle size and size distribution, which can differ substantially due to differences in the environment of the treatment plant, have a significant impact on pore blocking of membrane. According to *Lim et al. (2003)*, small particles affect fouling much more than large particles. In the MBR process, the flocs' median diameter is ten times smaller than in the CAS system and ranges from 4 to 40 μm (*Sombatsompop, 2007*). The reasons are high aeration and turbulence in the MBR (*Sombatsompop, 2007*) and/or shear forces caused by pumping during crossflow filtration (*Kim et al., 2001*), thus leading to the breakup of biological flocs. With respect to the particles or substances to be removed, the maximum pore size can be chosen, for example, with the aim of disinfecting the effluent (*Evenblij, 2006*).

Membrane materials also play a decisive role, since they may interact with substances in the feed flow. In order to minimize fouling by hydrophobic compounds, membrane materials, such as polymers, feature modified surfaces to provide the appropriate degree of **hydrophilicity** (*Judd, 2004*). Furthermore, *Zhang et al. (2006)* state that **membrane porosity** has an impact on the membrane adsorption process and the degree of this impact depends on adsorption system and membrane pore size. The porosity affects the concentration profile of the solute near the membrane surface on the liquid side, which leads to the reduction of the mass transfer area of the membrane. According to *Tang et al.*

(2007), flux reduction correlates with membrane **roughness**, with rougher membranes tending to experience more flux reduction than smoother ones.

2.4.4.2. Operating conditions

Regarding operating conditions, membrane **permeate flux** seems to be the key parameter controlling the fouling rate rather than membrane aeration and solids concentration (*Gui et al., 2003; Germain et al., 2005*). The need to maintain a high permeate flux is one of major cost factors - capital as well as operating costs - associated with submerged membrane systems. Previous studies showed that MBR operation at high flux rates, i.e. at high convection rates toward the membrane, leads to colloidal aggregation and the formation of cake layers on the membrane surface (*Chang et al., 2002; Sen Gupta et al., 2005*) and to irreversible adsorption of compounds to be removed only by chemical cleaning (*Le Clech et al., 2003*).

The introduction of the so-called critical flux concept, by *Field et al. (1995)*, has become the focus of many studies on submerged MBR. The hypothesis for MF is based on the existence of a flux start-up value, the critical flux, below which a flux decline (or an increase of TMP) with time does not occur. The operation below the critical flux, i.e. subcritical flux is expected to lead to little or even no irreversible fouling. The highest flux at which TMP remains stable is the critical flux and is influenced by parameters such as MLSS, membrane material, and system hydrodynamics (*Chang et al., 2002*). However, many authors believe that the concept of critical flux is not to be applied to MBRs. The reason appears to be the presence of colloidal and/or dissolved matter depositing onto or within the membrane at all fluxes greater than zero, thus causing measurable permeability decline even under sub-critical flux conditions (*Cho et al., 2002; Judd, 2006; Zhang et al., 2006*).

The **crossflow system** (see *chapter 2.6.1*) seems to have a major influence on membrane fouling besides permeate flux (*Germain et al., 2005*). Crossflow velocity (CFV) affects the mass transport of particles away from the membrane surface, thus preventing their accumulation, and promotes the back transport mechanisms (see *chapter 2.5.1*). CFV is generated by aeration, which not only provides oxygen to the biomass, but also maintains the solids in suspension and scours the membrane surface, and thus mitigates fouling (*Chang et al., 2002*). *Germain et al. (2005)* report that higher membrane aeration intensities result in lower membrane fouling rates, however, there is a limit beyond which there is little improvement despite further increasing gas flow. *Hong et al. (2002)* explain this phenomenon by an increase in the back transport of foulants from the membrane surface. Under specific conditions intermittent airflow can achieve better fouling control than continuous airflow at constant or lower net airflow rates (*Fane, 2005b*). The immediate effect of CFV is the shear stress on the membrane surface, which may be a measure of its effectiveness. However, in submerged systems it is difficult to calculate shear stress because of the discontinuous flow pattern near the membranes caused by air bubbles (*Evenblij, 2006*).

Another important operating parameter that tends to encourage fouling certainly is the **SRT, i.e. sludge age**. However, SRT cannot be considered as direct fouling cause, but rather as parameter influencing various sludge properties, such as floc size, settling characteristics, sEPS/SMP (soluble extracellular polymeric substances/soluble microbial products) content etc., characteristics that are directly related to fouling rates (*Al-Halbouni, 2008*). *Police et al. (2008)* report that there is a large difference in sludge filterability, membrane cleaning, and biological activity in MBR when the system is operated at SRT of 20 and 80 days. SRT is an important design parameter as it is directly linked to the net pro-

duction of excess sludge (see *chapter 2.3.4*). The most obvious impact of SRT variation is on MLSS concentration (*Chang et al., 2002*). Most studies show that a moderate to high SRT results in less membrane fouling (*Cicek et al., 2001; Grelier et al., 2006; Zhang et al., 2006*). Although there are many studies dealing with different aspects of SRT, studies giving more detailed insights into fouling mechanisms and their relation to SRT dependent parameters are still lacking. Many authors state a negative impact on membrane fouling by low SRT, generally, by high concentrations of SMP or bound EPS (*Rosenberger, 2003; Grelier et al., 2006; Drews et al., 2008; Malamis et al., 2009*). Carbohydrates, particularly the polysaccharide fraction in the supernatant, of SMP or soluble EPS are often considered as major cause of membrane fouling in MBR (see *chapter 2.4.4.3*) (*Judd, 2004; Grelier et al., 2006; Rosenberger et al., 2006; Pan et al., 2010*).

There are other factors that vary with SRT and thus influence fouling, such as dissolved oxygen (DO) concentration or sludge morphology. To mineralize SMP/sEPS, oxygen is required. *Drews et al. (2005)* conclude that unsteady states, such as shifts in oxygen supply, seem to result in increased EPS formation. *Lu et al. (2001)* report that a DO concentration below 1 mg/L leads to elevated EPS concentrations. Therefore, control of aeration in submerged MBR is essential. Furthermore, sludge morphology changes significantly with modified SRTs, going along with changes in sludge floc size and free water content and thus with the development of different microbial communities that may affect membrane fouling (*Meng et al., 2006; Al-Halbouni, 2008*). *Massé et al. (2006)* observed a decrease in floc size with higher SRTs. This was explained with the development of non-flocculating organisms producing less biopolymers responsible for the formation of floc aggregates. Moreover, better degradation and hydrolysis of macromolecules are provided at high SRTs.

2.4.4.3. Biomass characteristics

The composition of activated sludge, (see *Figure 2-8*), in a biological wastewater treatment process is very complex. Generally, activated sludge contains suspended particles (microorganisms, flocs, inert material), colloids and solutes (*Rosenberger et al., 2006*) that derive from feed water components and metabolites produced during biological reactions.

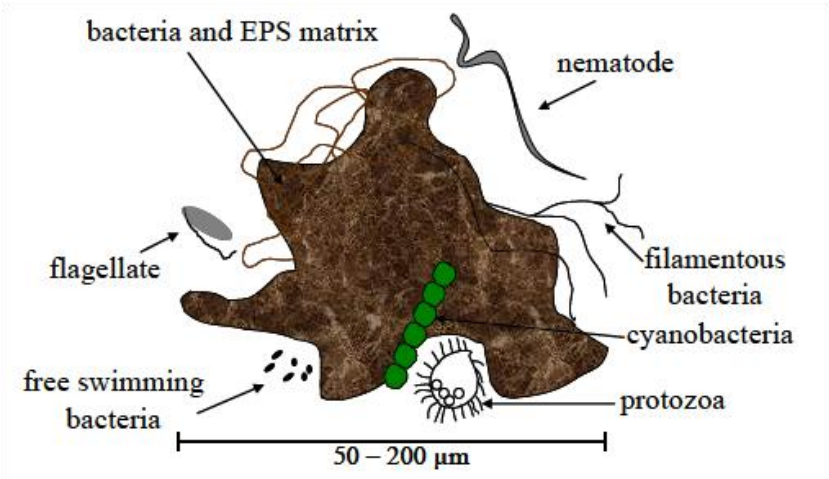


Figure 2-8: Scheme of an activated sludge floc with ambient microorganisms (*Al-Halbouni, 2008*).

Each of these components can affect the fouling process (*Chang et al., 2002*). However, due to the very heterogeneous nature of mixed liquor, the contribution of its individual components to membrane

fouling is discussed controversially in the literature. While some authors report a negative impact of particle concentration, i.e. suspended solids (SS) or (MLSS), on membrane fouling, some report positive ones and some none at all (*Cicek et al., 1998; Madaeni et al., 1999; Lee et al., 2001*). *Defrance et al. (2000)* report the biomass relative contribution on fouling to be 65, 30, and 5 % for the suspended solid fraction, colloids, and dissolved matter, respectively.

When considering the experimental setups, the general trend of MLSS increase on fouling in municipal applications seems to result in less fouling at very low MLSS concentrations (< 6 g/L), no impact at medium MLSS (8-12 g/L), and more fouling at very high MLSS concentrations (> 15 g/L) (*Rosenberger et al., 2005*). Others identified the soluble and colloidal fraction of activated sludge, also referred to as SMP, as the most significant factors responsible for membrane fouling (*Bouhabila et al., 2001; Cicek et al., 2003b; Rosenberger et al., 2006*).

Molecules or grain size distribution of soluble organic compounds in the liquid phase of activated sludge covers a wide range from nanometer to micrometer. According to *Howe et al. (2002)*, the impact of particulate material (larger than 0.45 μm) on fouling was almost negligible compared to soluble compounds smaller than 20 nm. Other authors (*Yuan et al., 2000; Fan et al., 2001*) show that high molecular weight (MW) compounds make a larger contribution to the fouling potential than low MW compounds, however, no author defined the upper size limit of compounds resulting in permeability decline.

In activated sludge models (ASM) of IWA, 0.45 μm filters act as indicator for screening particulates from colloids and solutes (*Henze et al., 1999*). However, it should be noted that there is no strict size classification of particulates, colloids, and solutes. *Howe et al. (2002)* define particulate matter, colloids, and dissolved organic matter (DOM) in the range of > 0.45 μm, 3-20 nm, and < 3 nm, respectively. *Jiang (2007)* differentiates macromolecular organic matter (MOM) from colloids, MOM to be in the range of 0.001-0.1 μm and colloids in the range of 0.1-1 μm. In this thesis, particulate matter, colloids, and truly dissolved matter are defined in the range of > 0.45 μm, 0.04-0.45 μm, < 0.04 μm, respectively.

Rosenberger et al. (2006) conclude that it is difficult to compare literature data, as MBR operating conditions and analytical methods differ. There are no standard methods for phase separation or the determination of the fouling potential. Methods used for phase separation are e.g. centrifugation, sedimentation, flocculation, and filtration. The fouling potential is determined both in batch trials and by analyzing online data of the respective modules in the MBR.

Soluble microbial products (SMP) and extracellular polymeric substances (EPS) are the mostly frequently used terms for compounds found responsible for membrane fouling in the MBR (*Nagaoka et al., 1996; Chang et al., 2002; Drews et al., 2007*). However, there is no clear distinction between SMP and EPS.

In general, EPS can be classified according to the activated sludge phase, i.e. bound EPS is associated with flocs and soluble EPS is present in the liquid phase of activated sludge (soluble and colloidal fraction) (*Jiang, 2007*). SMP and soluble EPS are organic macromolecular microbial derivation products. According to *Laspidou and Rittmann (2002)*, they do not differ from each other. Due to their complexity, soluble EPS and SMP solutions are both characterized via the following sumparameters, i.e. protein and carbohydrate (mainly compounds such as polysaccharides) (*Fan et al., 2006; Rosenberger et al., 2006; Wang et al., 2006*), chemical oxygen demand (COD) concentration, and total organic carbon (TOC) level (*Huang et al., 2000; Rosenberger et al., 2005*). Since there are no standard methods for

separating the water phase from the biomass and for analyzing SMP and EPS, the comparison of results between research groups is difficult and leads to contradiction.

In this thesis, SMP and soluble EPS are generally called biopolymers and in order to determine their fouling potentials, they are analyzed with photometric (protein, polysaccharide, COD, TOC) and chromatographic methods (see *chapter 5*).

There are further parameters associated with the particulate fraction that are reported to influence membrane performance. These are **particle size distribution** (see *chapter 2.4.4.1*), **sludge hydrophobicity** (*Chang and Lee, 1998; Meng et al., 2006*), **sludge viscosity** (*Nagaoka et al., 1996; Günder, 1999*), and **dewaterability** (*Wang et al., 2006; Wang et al., 2008*)**.**

Hydrophobic flocs lead to high flocculation propensity of sludge. Some authors found that highly hydrophobic flocs can have an impact on membrane fouling (*Chang and Lee, 1998; Meng et al., 2006*). EPS concentration and the presence of filamentous bacteria in sludge directly influence the relative hydrophobicity in the biomass floc. *Meng et al. (2006)* report that excessive growth of filamentous bacteria resulting in a much higher release of EPS, higher hydrophobicity of sludge flocs, and more irregularly shaped flocs are responsible for severe membrane fouling. In another example, foaming sludge showed a 100 times greater flux decline than non-foaming sludge. The increase was attributed to the hydrophobic and waxy nature of the foaming sludge surface (*Chang and Lee, 1998*).

The dewatering or filterability of sludge can be characterized by the capillary suction time (CST). The CST test determines the rate of water released from sludge (*Sombatsompop, 2007*). A high value of CST usually implies poor filterability and dewaterability of sludge (*Chen et al., 1996*). Some researchers report that CST has a significant influence on membrane fouling, more than other sludge variables, such as viscosity, MLSS, and proteins in the mixed liquor (*Wang et al., 2006; Wang et al., 2008*) and was also found highly related to the amount of SMP (*Pan et al., 2010*) and polymeric substances such as carbohydrates and EPS (*Jin et al., 2004*). Due to its significant correlation with membrane fouling, simple equipment, and short time required, CST could be one of the most effective and convenient sludge variables for evaluating sludge properties and membrane fouling in submerged MBRs (*Wang et al., 2006*).

Viscosity describes a fluid's internal resistance to flow and is determined as a function of shear rate [s^{-1}] and shear stress [Pa]. The correlation between the shear rate and shear stress is presented in the form of a flow curve. According to *Rosenberger (2003)*, viscosity proprieties of activated sludge are influenced by sludge concentration. In general, the rheological prosperities of activated sludge are reported to be pseudoplastic (non-Newtonian) in nature (*Lotito et al., 1997*) or pseudoplastic with initial yield stress (*Slatter, 1997*), suggesting that sludge viscosity decreases with shear rate. Pseudoplastic behavior can be explained by the bioparticulate structure of activated sludge. The biomass particles tend to flocculate resulting in a large-scale of flocs network. This structure is disrupted with increasing shear rate, resulting in a decrease in viscosity. High MLSS concentrations might be expected to have a profound influence on MBR performance owing to its effect on both the dynamic cake layer thickness and viscosity. The formation of flocs or other cell aggregates is provided by EPS, which form a highly hydrated gel, keeping the microorganisms together. Sludge viscosity has been reported to increase also with EPS concentration (*Nagaoka et al., 1996; Günder, 1999*). The correlations between shear rate, shear stress, and optionally yield stress (non-Newtonian fluids) are described by the mathematic regression analysis. *Table 2-3* shows mathematical models (Newton, Oswald de Waele, und Herschel-Bulkley) often used to describe the rheology of sludge.

Table 2-3: Rheological standard models with viscosity functions.

Model	Equation of state	Apparent viscosity	Parameters	Function
NEWTON	$\tau = \eta \cdot \gamma^n$, n=1	$\eta_{dyn} \neq f(\gamma)$	1 (linear)	Ideal viscous flow behavior
OSWALD DE WAELE	$\tau = K \cdot \gamma^n$, n<1	$\eta_s = f(\gamma) = K \cdot \gamma^{n-1}$	2 (non-linear)	Structural viscous behavior without yield stress
HERSCHEL-BULKLEY	$\tau = \tau_0 + K \cdot \gamma^n$, n<1	$\eta_s = \frac{\tau_0}{\gamma} + K \cdot \gamma^{n-1}$	3 (non-linear plastic)	Flow curve with apparent yield stress

Temperature is a well-known factor influencing the kinetic parameters of biological processes and plays a significant role during degradation processes and thus for wastewater treatment. Many researchers have already observed the temperature impact on the fouling behavior (*Barker et al., 1999, 2000; Jiang et al., 2005; Rosenberger et al., 2006; Drews et al., 2007*). It is also believed that SMP is produced as a response to environmental stress imposed on microorganisms, enhanced at low temperatures (*Schiener et al., 1998*).

2.5. Modeling of membrane filtration processes

In this chapter, the processes of diffusive and hydrodynamic mass transfer, i.e. hydraulic resistance due to membrane material, concentration polarization, pore blocking, and adsorption are described. The accumulation of rejected material near the membrane surface (concentration polarization) or on the membrane (cake or gel layer buildup) leads to an increased hydrodynamic resistance to solvent flow through the membrane (see *chapter 2.4.3*). During operation, these processes contribute significantly to the decline in permeate flux and/or increase in the pressure drop.

In order to describe or predict the permeate flux decline in membrane filtration, different models are used that involve different mass transfer mechanisms for estimating cake layer formation and concentration polarization. Valuable reviews on ultrafiltration and microfiltration models, for example, are offered by *Belford et al. (1994)* and *Bowen and Jenner (1995)*. In the following paragraphs, the existing models referring to “film theory” (*Belford et al., 1994*), gel polarization, and resistance in series are reviewed.

2.5.1. Diffusive mass transfer - concentration boundary layer

Due to the rejection of suspensions of fine particles and solutes near the membrane surface, the concentration in the boundary layer will gradually increase (see *Figure 2-9*). In a certain distance (δ) from the membrane surface, complete mixing is assumed resulting in a constant bulk concentration (c_b). In the laminar boundary film layer, with the thickness (δ), the concentration (c) is increasing due to the convective solute transport in direction (x) of the flux and reaches a maximum value at the membrane surface (c_m) (*Beier, 2007*).

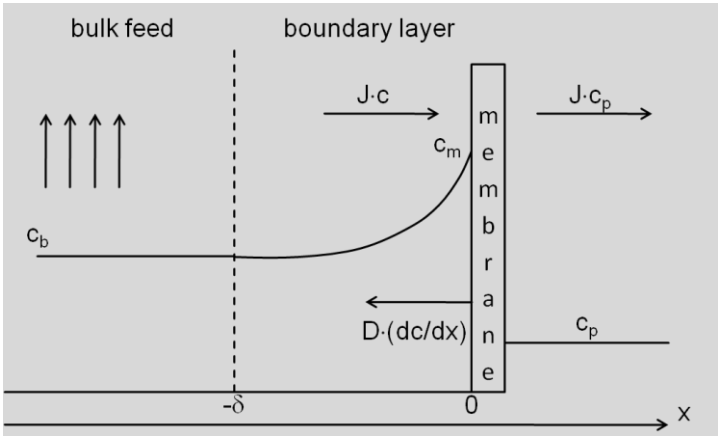


Figure 2-9: Boundary layer formation (concentration polarization) in ultrafiltration (*Beier, 2007*).

The convective flow of solutes toward the membrane surface may be expressed as J·c, whereas the flow of not fully retained solute through the membrane equals $J \cdot c_p$ (*Mulder, 2000*). The accumulation of solutes in the boundary layer creates a concentration gradient. This convective transport is counter-balanced by the diffusive transport of solutes back into the bulk solution and the fraction of the solute that passes the membrane. This condition can be achieved only if the solute concentration at the membrane wall is higher than that in the bulk solution. It should be noted that only the phenomena of concentration polarization are considered here with fouling being excluded.

The solute mass balance in the laminar boundary film layer can be described via the Fick's first law (Fickian diffusion) (*Mulder, 2006; Beier, 2007*).

$$J \cdot c + D\frac{dc}{dx} = J \cdot c_p \tag{2.13}$$

with:
D - diffusion coefficient, [m^2/s]
dc/dx - concentration gradient in the laminar boundary film layer, [$kg/(m^3 \cdot m)$]
c - solute concentration, [mol/L, kg/m^3]

The boundary conditions are:
$x = 0 \Rightarrow c = c_m$
$x = -\delta \Rightarrow c = c_b$

The mathematical description of steady-state permeation under these conditions is commonly known as "film theory" (*Belford et al., 1994*). The integration of the *equation 2.6* results in (*Mulder, 2000*):

$$\frac{c_m - c_p}{c_b - c_p} = \exp\left(\frac{\delta \cdot J}{D}\right) = \exp\left(\frac{J}{k}\right) \tag{2.14}$$

The ratio of the diffusion coefficient (D) and the thickness of the boundary layer (δ) can be replaced by mass transfer coefficient (k), which describes the back-diffusion of solutes from the boundary layer

towards the bulk solution. Since c_m and c_b are constants for a given solution, the limiting flux (J) can only be increased by increasing k. The mass transfer coefficient (k) is related to the Sherwood number (Sh) (*Mulder, 2000*):

$$Sh = \frac{k \cdot d_h}{D} = a \cdot \mathrm{Re}^b \cdot Sc^c \cdot \left(\frac{d_h}{L}\right)^d \tag{2.15}$$

with:
Re - Reynolds number
Sc - Schmidt number
a, b, c, d - constants
d_h - hydraulic mean diameter of the feed channel, [m]
L - length of the feed channel, [m]

In the film theory model, the back-diffusion of particles is based on Brownian diffusion, hence the diffusivity D is given by the Stokes-Einstein relationship (modified after *Wett, 2005*):

$$D = \left(\frac{k_B \cdot T}{3 \cdot \pi \cdot \eta \cdot d_p}\right) \text{ [m}^2\text{/s]} \tag{2.16}$$

with:
T - absolute temperature, [K]
k_B - Boltzmann constant ($1.3807 \cdot 10^{-23}$), [J/K]
d_p - sphere diameter, [m]
η - dynamic viscosity of the permeate, [Pa·s]

Furthermore, during filtration of high-molecular solutes, the boundary layer finally reaches a maximum concentration where a solid gel is built at the membrane surface. This way, the upper limit for the permeate flux is reached, since the gel concentration (c_g) is the highest possible solute concentration. The assumption of complete solute rejection and forming the steady state mass balance of the solute in the boundary layer leads to a simple correlation for the limiting permeate flux (*Michaels, 1968*):

$$J_{\lim} = k \cdot \ln\left(\frac{c_g}{c_b}\right) \tag{2.17}$$

with:
k - mass transfer coefficient, [m/s]
c - solute concentration, [mol/L, kg/m^3]

This Michaels's correlation is also called the gel polarization model and has been extensively used in the analysis of experimental macromolecule ultrafiltration data.

2.5.2. Hydrodynamic particle transport – cake buildup

However, colloidal suspensions, and their behavior at the membrane surface during filtration, can no longer be described via diffusive mass transport models, but rather with hydrodynamic models. Several transport mechanisms interact to bring particles close to the membrane surface or to transport them away from the membrane into the bulk solution. Particles being arranged sufficiently close to the membrane surface deposit in case the decisive forces (see *Figure 2-10*), acting on suspended particles, favor attachment to the membrane or to previously deposited material (*Chellam and Wiesner, 1992*).

Altmann and Ripperger (1997) distinguish the forces on streaming and deposited particles. On streaming particles only hydrodynamic forces act, while on deposited particles there are additional adhesive and friction forces between the particles and the contact surface.

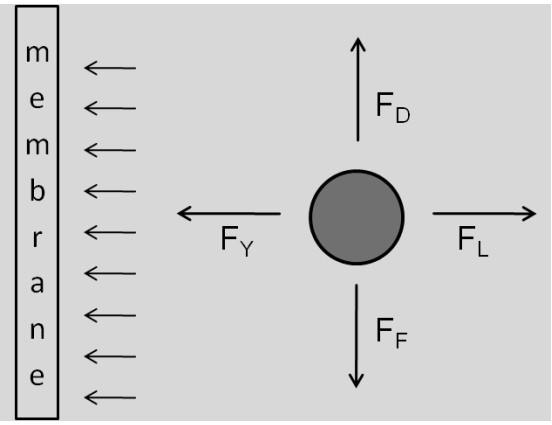


Figure 2-10: Forces acting on a single particle (modified after *Altmann and Ripperger, 1997*).

Under defined hydrodynamic conditions, i.e.

- The flow in the channel is mostly turbulent
- The size of the filtrated particles is usually smaller than the thickness of the laminar boundary layer
- Close to the membrane, the crossflow velocity w(y) increases linear with the distance to the membrane (y), the following forces can be described: F_y – drag force of the filtrate flow, F_D – drag force of the crossflow, F_L – lift force, F_F – friction force.

Furthermore, *Altmann and Ripperger (1997)* report that it is mainly the balance between the lift force and the drag force of the filtrate flow that determines the layer formation at the membrane. This means, at high filtration rates the drag force of the filtrate flow is higher than the lift force, hence the particles are transported to and deposited on the membrane surface. At low Reynold numbers, the drag force of the permeate flow (F_Y) can be estimated with the Stockes equation:

$$F_Y = 3 \cdot \pi \cdot \eta \cdot x \cdot v_F \text{ [N]} \qquad (2.18)$$

with:
η - dynamic viscosity of the permeate, [Pa·s]
x - particle size, [m]
v_F - filtration rate, filtrate flow, flux, [L/(m^2·h)]

Since the Stockes equation (*2.18*) considers only very low particle concentrations without particle interaction, it is necessary to add a correction factor (λ) that depends on particle size (x), particle size distribution ($q_3(x)$), and on the volume concentration (φ_s).

Moreover, the attachment of particles to the membrane is caused by the large influence of the adhesive forces, i.e. van der Waals forces and electrostatic interactions that, in most cases, lead to irreversible processes.

$$F_{vdw} = \frac{h\varpi \cdot x}{32 \cdot \pi \cdot a^2} \text{ [N]} \tag{2.19}$$

with:
$h\varpi$ - Lifschitz-van der Waals constant, [eV]
a - adhesive distance (0.4 nm), [nm]

However, the estimation of these forces is complicated because of many parameters influencing the adhesive forces.

2.5.3. Membrane mass transfer resistance

The most common way to model MF/UF processes is by the resistance-in-series approach. This model assumes a correlation between permeate flow, concentration polarization (R_{cp}), fouling (R_f), and membrane resistance (R_m). Hydraulic resistance is the result of material accumulation on the membrane surface and/or in the membrane pores. The fouling resistance (R_f) is the sum of resistance due to adsorption (R_a), pore blocking (R_p), and gel/cake layer formation (R_g). Using Darcy's law as a theoretical basis, the flux decline can be determined by (*AWWA, 2005*):

$$J_p = \frac{1}{A_M} \cdot \frac{dV_p}{dt} = \frac{\Delta p}{\eta \cdot \left(R_m + R_{cp} + R_f\right)} \text{ [L/(m}^2\text{·h)]} \tag{2.20}$$

with:
J_p - permeate flux, [L/(m^2·h)]
A_M - membrane surface, [m^2]
V_p - volume of permeate, [L]
t - operation time, [h]
Δp - transmembrane pressure, [bar]
η - dynamic viscosity of the permeate, [Pa·s]

Membrane controlled mass transfer provides the simplest operational condition for porous membrane systems in the absence of fouling, with pressure as driving force (*Stephenson et al., 2000*).

R_m is the membrane intrinsic resistance characterized mainly by pore shape and size and membrane thickness, as determined during the manufacturing process (*Chang and Kim, 2005*). R_f depends on operation time, transmembrane pressure and crossflow velocity (*Rosenberger, 2003*).

$$R_m = \frac{S^2 \cdot (1-\varepsilon)^2 \cdot K \cdot \tau \cdot \delta_p}{\varepsilon^3} \text{ [1/m]} \quad (2.21)$$

with:
ε - porosity (or voidage), [-]
η - dynamic viscosity of the permeate, [Pa·s]
S - specific area (surface area per unit volume), [m^2/m^3]
τ - tortuosity, [-]
δ_p - thickness of the porous layer, [m]
K - constant equal to 2 for perfectly cylindrical pores, [-]

However, during membrane operation with real feed, membrane resistance may be only a small part of the total resistance, usually negligible. Resistance is usually measured via a series of filtration experiments comprising pure water filtration, sludge filtration, and pure water filtration following filter cake removal (*Chang et al., 2002*). Adsorption resistance (R_a) is caused by adsorption on the membrane surface or pores and occurs independently of flux. For measuring this variable, for a certain time (usually a few hours) the membrane is brought into contact with the feed in the absence of flux. Then, a pure solvent flux at a known TMP is measured. The experiment can be repeated for other contact times. Other resistances, such as concentration polarization (R_{cp}), pore blocking (R_p), and gel/cake layer formation (R_g), are estimated during the operation with feed, via the solvent transport through the membrane (*Peinemann and Nunes, 2010*). However, the validity of differentiating between various resistance components on the basis of arbitrary physical tests is questionable (*Chang et al., 2002*). Therefore, *Gander et al. (2000)* prefer to estimate a single resistance value, i.e. R_f, including all resistances except the clean membrane.

2.6. Strategies for fouling reduction and improved membrane performance

MBR performance is generally assessed by two parameters, the biological treatment capacity of the bioreactor and the hydraulic membrane efficiency in terms of permeability. In order to ensure the required hydraulic performance of MBRs in municipal wastewater treatment, there is a choice of several measures to be considered if need be.

There are a number of commonly used cleaning techniques and strategies for the removal of fouling layers, such as backwash with permeate, relaxation breaks, membrane surface scouring by using gas bubbles in a liquid (crossflow), chemical cleaning, and any combination thereof. Moreover, coagulation/flocculation and adsorption processes as well as the application of expanded clay or Kaldnes® elements are discussed. The method of choice for fouling control must be technically and economically feasible, upgradeable to production size, and well suited for cleaning in place.

2.6.1. Control of filter cake buildup – Crossflow aeration system

Fouling control of the filter cake buildup in MBRs is achieved by an additional “crossflow” aeration system from below the membrane unit (see *chapter 2.3.1*). The commonly applied coarse-bubble crossflow system provides high levels of air turbulence and shear forces that scour the membrane surface, thus removing solids particles attached and preventing irreversible fouling. In order to generate a

high liquid shear velocity, the air flow rate of coarse-bubble aeration is more than twice compared to fine-bubble aeration systems (*Krause, 2005*).

As crossflow aeration is the largest energy consumer in MBRs (0.5-1.2 kWh/m^3 permeate) (*DWA, 2007a*), many MBR manufacturers and researchers engage in the optimization of membrane air scour energy (*Engelhardt, 2003; Krause, 2005; Fane, 2005b*). The cake removing efficiency was improved by intensifying the air flow without increasing the air flow rate (*Ueda et al., 1997*). Therefore, it was suggested to stack several membrane modules over a smaller floor area in order to enhance the aeration intensity and to decrease the aeration demand. Moreover, *Cui et al. (2003)* report that slug or plug flow provides maximum efficiency for promoting flux.

In practice, membrane aeration values are based on experience and usually recommended by the membrane's manufacturer. Aeration rates from pilot and full-scale studies are rather taken than theoretical ones, since the calculation of the relationship between aeration and flux decline is arguable and yet not fully understood (*Judd, 2006*). The key parameter to calculate the energy demand of submerged MBRs is the specific aeration demand, i.e. the ratio of the air flow rate (Q_f) either to the membrane area (SAD_m), as individual membrane element, or the permeate volume (SAD_p). Current membrane systems are operated in the range of 0.2-0.8 $Nm^3/(m^2 \cdot h)$ (*Judd, 2006; Guglielmi et al., 2008; Verrecht et al., 2008; Lorain et al., 2010*), normalized to 20 °C, since the air flow is temperature dependent.

2.6.2. Membrane cleaning

2.6.2.1. Physical cleaning (backwash with permeate, relaxation)

Backwashing (or backflushing) is a physical measure of intermittent cleaning or partial recovering of fouled membranes. In a backflushing procedure, a slight overpressure is applied to the permeate side of the membrane, forcing solution from the permeate side to the feed side of the membrane. The flow of solution removes deposited material from the surface, this kind of fouling therefore generally called “reversible” fouling. This method is commonly used to clean submerged hollow-fiber membrane modules that can withstand reverse permeate flow without damaging the membrane. In flat-sheet membrane modules, backwashing is usually not applied because of damage risk. However, there is an exception, a new membrane module (Bio-Cel®), developed by Microdyn-Nadir, that ensures efficient backwashing of the membrane (see *chapter 2.3.2*) without damage.

Relaxation refers to the periodical break of the filtration process and thus allows for the removal of deposited foulants from the membrane surface by diffusive back transport in “relaxed” conditions. This process is further enhanced by the shear created by air scouring (*Chua et al., 2002*). Relaxation can be easily implemented in all MBR configurations (*Jiang, 2007*). In contrast to backflushing, there is no demand of permeate.

During backflushing and relaxation, applied at the end of each filtration cycle, membrane scouring with air bubbles is continued. In order to avoid membrane damage, backflushing has to be performed with great care. Interval between backflushing periods usually is in the range of a few minutes. Membrane suppliers normally provide information on backwash and relaxation procedures (frequencies, flux, etc.) required for their systems. As variations in backflush frequency and flux as well as the duration of relaxation periods have an impact on the system's productivity, these parameters should be optimized during pilot testing to provide the most economical process.

2.6.2.2. Chemical cleaning

Since physical measures alone are often not effective enough to maintain sufficient flux and minimize the rate of long-term irreversible fouling, chemical cleaning is required for restoring membrane permeability. Efficient chemical cleaning requires the selection of cleaning agents that target dominant compounds responsible for fouling and that do not adversely affect the membrane itself. Moreover, the chemical should loosen and dissolve the foulant, keep the foulant in dispersion, and avoid new fouling. Thereby, a good knowledge of fouling mechanisms is essential.

The commonly used chemical reagents normally belong to one of five categories (with some overlapping): caustic solutions (e.g. sodium hydroxide), acids (e.g. citric acid), oxidative agents (e.g. sodium hypochlorite), surfactants, and enzymes (*Arnal et al., 2009*). Caustic solutions and oxidants are used to clean membranes fouled by organic and microbial foulants, whereas acid agents are effective in eliminating mineral fouling. Surfactants affect fouling dominated by the formation of biofilms, whereas enzymes are used to solubilize the organic matrix of a fouling layer (*Poele and van der Graff, 2005*).

There are two procedures in use for chemical cleaning:

- **In-situ**, called cleaning in place (CIP)
  Membrane modules are cleaned while either being submerged in activated sludge or with the membrane tank drained, the latter called “cleaning in air” (CIA).
  In-situ is a maintenance cleaning that usually takes 30-60 minutes for a complete cycle and is repeated every 3-7 days at low reagent concentrations of 200-500 mg/L NaOCl for classical MBRs (*Judd, 2006*). Chemicals are introduced to the permeate during backward flush.
- **Ex-situ**, i.e. cleaning out of place (COP)
  This intensive cleaning procedure is carried out either in the drained membrane tank or in an external tank. Ex-situ cleaning is generally performed in case the TMP reaches a maximum allowable mechanical membrane resistance to regain most of its permeability. During intensive cleaning, membrane modules are submerged into chemical reagents for soaking, thus employing higher reagent concentrations than with in-situ cleaning.

Physical and chemical cleaning methods as well as chemical reagents are often combined. Organic compounds can be removed either with CIP or COP, under the addition of oxidants such as NaOCl, while the removal of inorganic compounds is best with citric acid. The efficiency of the cleaning method used depends on many factors, such as reagent concentration, process temperature, contact time of chemicals, and flux. In practice, the most suitable methods are determined by trial and error (practice tests).

Though chemical cleaning methods are routine and successfully employed to recover some of the flux, nonetheless there are negative aspects to be considered, such as high consumption of hazardous chemical agents, manpower requirement, energy consumption, and downtime periods that increase the operating costs. Current research focuses on new cleaning strategies, particularly on the avoidance of chlorinated by-products caused by using chlorinated oxidants, and the reduction of membrane material damage caused by using oxidizing chemicals (see *chapters 2.6.2.4*).

2.6.2.3. Physical-chemical processes

Physical-chemical processes, such as adsorption and coagulation, have been used in the pretreatment step for a long time. These processes can be realized as a step prior to membrane filtration or in combination with MBR process as hybrid system for the removal of pollutants from wastewater.

Adsorbent dosage in MBRs, e.g. with powdered activated carbons (PAC), to alleviate fouling has been studied comprehensively (*Kim and Lee, 2003; Li et al., 2005; Vigneswaran et al., 2007*). It was reported that PAC adsorbs and degrades soluble organics, thus effectively reducing SMP and EPS levels and leading to enhanced permeability (*Kim and Lee, 2003*). Similarly, *Vigneswaran et al. (2007)* state that the PAC addition directly into the submerged MBR keeps the organic removal efficiency constant without the need for the membrane to be cleaned for a long time. *Li et al. (2005)* observed a low fouling potential and an increase in critical flux by 32 % at a PAC concentration of 1.2 g/L. However, there was no significant improvement in the filtration performance in case PAC was dosed only once and without sludge wastage in the bioreactor (*Ng et al., 2006*). According to *Fang et al. (2006)*, the performance of membrane filtration can be improved by only dosing PAC in regular intervals. Optimal selection of the PAC type to be used in the hybrid system is important, in order to minimize the PAC dose and to enhance the performance (*Thiruvenkatachari et al., 2004*).

Yoon et al. (2004) studied the efficiency of a new membrane fouling reducer. They report on the significant flux enhancement in MBR by adding a cationic polymeric material. The flux enhancement was explained by the increase in floc size and the reduction in SMPs in the bulk solution. *Itonaga et al. (2004)* found out that the dosage of ferric compounds reduces irreversible fouling and controls suspension viscosity.

2.6.2.4. Alternative cleaning methods – mechanical cleaning

In place of regular cleaning with chemical agents, mechanical membrane cleaning may be used, particularly if chemical cleaning does not restore membrane flux.

Another method to remove fouling deposit or concentration polarization is mechanical cleaning. *Lowe and Durkee (1971)* studied the mechanical cleaning in large tubular membrane modules through "scouring balls". The cleaning action is obtained by rolling balls in the channels between the membranes. Some authors reported that the use of **turbulence promotors** minimize or control concentration polarization (CP) and membrane fouling through the enhancement of the convective flow and the generation of turbulences due to the introduction of turbulence promoters in the flow conduit (*Van der Velden, 1976; Van der Waal et al., 1977; De Boer et al., 1980; Rios et al., 1987; Noordman, 2000*). Moreover, turbulence promotors continuously strike the membrane surface and thereby prevent the occurrence of CP and membrane fouling and also remove the matter that has already been deposited. *Rios et al. (1987)* considered the use of fluidized bed technique for tubular membrane modules in order to minimize membrane fouling. They stated that use of turbulence-promoting agents resulted in a significant increase of permeate flux through the membrane. However, all above mentioned experiments were only conducted for tubular modules and not for submerged flat sheet membranes.

Wulf and Orth (2008) investigated another mechanical cleaning procedure for MBR. They introduced **carrier elements** into filtration tanks with submerged flat sheet membranes to swirl and clean the membrane during filtration. The cleaning elements were polyurethane foam cubes with a size of 3-5 mm and polyethylene Kaldnes® and Rauschert (Bioflow 9) carriers of 9-10 mm. The fluidized carrier

elements partly removed membrane fouling, thereby increasing the membrane's performance. However, the study also showed that the introduced carriers damage the membrane and require a big enough gap between membrane plates (> 10 mm), i.e. needing a low packing density of membranes.

Another method to minimize membrane fouling is the application of **expanded clay**. *Klegraf (2006)* carried out experiments with an expanded clay material (Liapor®) to act as abrasive inorganic material. However, due to its hygroscopicity, the Liapor® material settled, making a further dosage necessary in order to maintain constant concentrations. Klegraf reports that by successively increasing the expanded clay concentration, an improvement in the filtration efficiency from 20 % to 75 % was observed.

3. General objectives and approach

As already mentioned in *chapter 1.1*, the performance of MBR systems is greatly influenced by the impact of fouling processes. The overall result is that membrane permeability declines and thereby increases operating costs.

Chemical cleaning, performed for fouling control and prevention, involves some negative aspects, inter alia, high demand for cleaning agents, enhanced manpower requirements, shortening of the membrane lifetime (damage by oxidizing chemicals), and not being environment friendly. Moreover, it is evident that in practice the decline of the permeability proceeds though chemical cleanings are performed periodically, mostly weekly.

Since physical and chemical measures alone are often not effective to maintain sufficient flux and additional shut down periods increase operating costs, the objective of this thesis is to develop practice-oriented, chemical-free, low-maintenance, and environment-friendly cleaning strategies for fouling reduction and hence decrease operating and maintenance costs of the MBR process.

The main focus of the present work is to develop a concept of mechanical cleaning by granulates for the enhancement of the MBR performance.

After being introduced into a loop reactor, the granulate acts as abrasive and should continuously scrub the membrane via the upward flow alongside its surface, forced by crossflow air, thereby removing the cake layer.

One of the most critical aspects of using membrane technology is to ensure that the membranes are intact and meet the membrane's functional requirements of biomass separation.

On the one hand, the long-term performance of MBR at high flux by using granular material in the treatment of municipal and synthetic wastewater is to be examined, and on the other hand, potential damages of the membrane surface resulting from the application of abrasive materials are to be monitored.

There are several methods that can be used to control membrane integrity including the control of water quality (turbidity, COD, total coliforms, E. coli, etc.). Moreover, the membrane material is to be examined on possible deformation or damage by means of REM images.

In addition to mechanical cleaning by granulates other concepts are to be investigated:

- The impact of membrane backwash, using a salt brine solution, on membrane performance
- The impact of chemical and physical cleaning (relaxation breaks) on membrane performance
- The effect of changed milieu conditions (aerobic, anaerobic) on membrane fouling
- The optimization of the crossflow aeration system with regard to the energy demand

The newly developed practice-oriented methods raise many questions:

- How to implement the process procedure?
- What are the interactions arising in connection with the membrane operation?
- What costs are to be expected?
- What are the pros and cons compared to other methods?
- What potential areas of aplication for the new methods are there?

In addition to the study on fouling reduction, questions on permeability loss in MBRs are to be answered:

(1) The influence of sludge characteristics (colloidal matter, viscosity, MLSS, CST, etc.), and operating conditions (temperature, SRT) on membrane fouling

(2) The effect of "truly soluble" matter (material passing the membrane with nominal pore size of approximately 0.04 μm) on membrane fouling

To accomplish these aims and to answer the consequential questions, pilot-scale experiments and batch tests are to be carried out. The results obtained in this work should provide new insights into fouling prevention and reduction in the MBR process.

4. Materials and methods

This chapter describes the materials and methods applied to develop strategies for fouling minimization in submerged membrane filtration.

4.1. Overview of experiments and plants

Four MBR pilot plants were operated in order to achieve information on their biological, hydraulic, and physical performance, later to be transferred to full-scale plants. In addition, further experiments were carried out in batch mode.

Below, the test facilities and their respective scopes are presented:

- MBR pilot plant (A) on the site of the municipal WWTP Süd in Darmstadt-Eberstadt
  - Investigation of the influence of sludge characteristics and operating conditions on membrane fouling
  - Investigation of the impact of membrane backwash, using a salt brine solution, on membrane performance
  - Investigation of the impact of chemical cleaning on membrane performance
  - Investigation of the effect of long-term relaxation breaks on membrane performance
- MBR pilot plant (B) on the site of Microdyn-Nadir in Wiesbaden-Biebrich
  - Application of mechanical cleaning with granular material in order to minimize the formation of fouling layers
  - Determination of the effect of “truly soluble” matter in wastewater and activated sludge on membrane fouling
  - Investigation of the effect of changed milieu conditions (aerobic, anaerobic) on membrane fouling
  - Investigation of the impact of chemical cleaning on membrane performance
- MBR pilot plant (C) on the site of the municipal WWTP in Wiesbaden-Biebrich
  - Application of mechanical cleaning with granular material in order to minimize the formation of fouling layers
- Pilot plant (D) on the site of the Technische Universität Darmstadt
  - Optimization of the crossflow aeration system with regard to the energy demand

4.1.1. MBR plant (A) in Darmstadt-Eberstadt

4.1.1.1. Plant set-up

Pilot plant (A) is situated on the testing site of the Institute IWAR (Technische Universität Darmstadt) at the municipal WWTP Süd in Darmstadt-Eberstadt (see *Figure 4-1*). The modular MBR system consists of an activated sludge tank with an integrated submerged flat-sheet membrane module of Microdyn-Nadir, Germany. The outline data of the membrane module are presented in *Table 4-1*. Each operation sequence includes forward filtration (420 s), relaxation (60 s), backwash (30 s), and relaxation (60 s).

The load volume of the activated sludge tank can be varied by changing the liquid level. During the test phases with high sludge ages, the volume was 7.6 m^3 at a liquid level of 3.3 m; at lower sludge ages, the volume was 4.6 m^3 at a liquid level of 2 m.

The plant was operated with mechanically pretreated (screen and grit chamber) municipal wastewater of the WWTP Darmstadt-Eberstadt. The wastewater was first separated from coarse particles by a fine sieve (gap width 0.5 mm). From a storage tank, the wastewater was then discontinuously pumped into the MBR system.

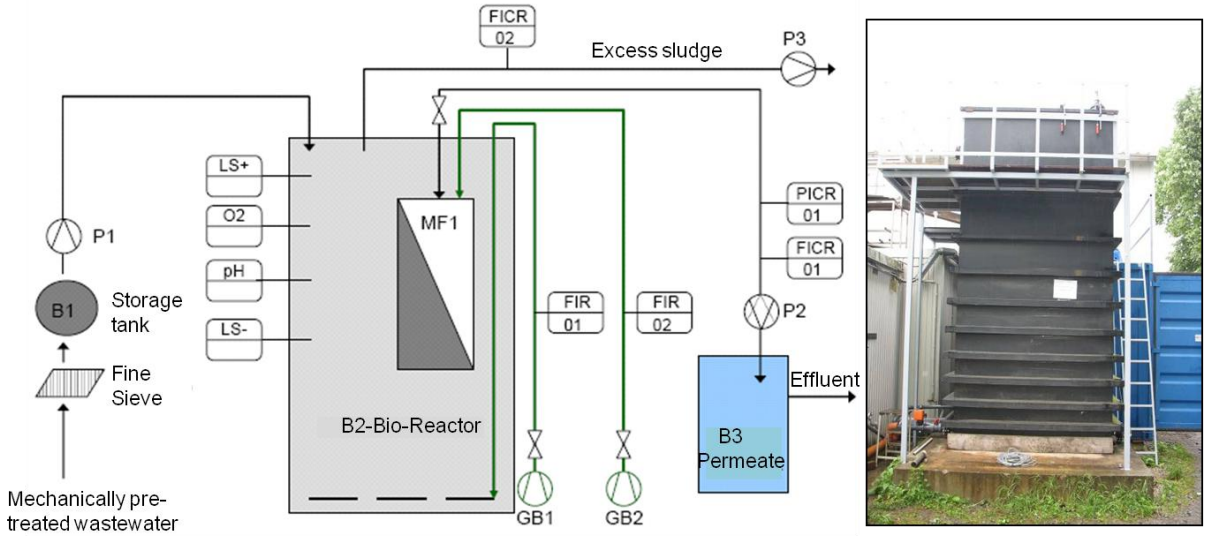


Figure 4-1: Flow sheet and illustration of the MBR plant (A) in Darmstadt-Eberstadt.

The MBR plant features two aeration systems: A fine-bubble aeration system to provide sufficient oxygen supply for biological processes is located at the bottom of the aeration tank. This aeration system consists of 4 aeration diffusers made of silicone membranes of Ott-System, Germany. Secondly, a standard crossflow system is placed directly beneath the membrane module in order to control the formation of filter cakes at the membrane surface. The fine-bubble crossflow aeration system consists of 9 aeration pipes (slits: 1 mm, gap between slits: 2 mm) with variable air outlet openings. This aeration system was continuously operated, the specific aeration demand per membrane area SAD_m being between 0.6 and 0.8 $m^3/(m^2 \cdot h)$.

Table 4-1: Characteristics of the membrane material.

Parameter	
Membrane material	Polyethersulfone (PES)
Membrane area	50 m^2
Nominal pore size	ca. 0.04 μm
Molecular weight cut off (MWCO)	150 kDa
Dimensions	1385 x 714 x 1585 mm

For venting the permeate pipe, a manually operated deaeration vessel was installed. In addition, the plant was equipped with an automatically operated excess sludge solenoid valve. The integrated pro-

grammable logic controller (PLC) enabled the MBR plant to be operated fully automatically, however, if required, the plant could also be operated manually. Data continuously measured during the operation (TMP, permeate flow, temperature, liquid level in the MBR tank, oxygen concentration, etc.) were stored on a computer for evaluation.

4.1.1.2. Experimental schedule

Table 4-2 gives an overview of experiments conducted at the MBR pilot plant (A) in Darmstadt-Eberstadt. The investigation on the influence of sludge characteristics and operating conditions on membrane fouling were carried out over the whole test period of 723 days. Between the 605th and the 723rd day, the investigation on the impact of backwash with a salt brine solution on membrane performance was conducted.

Table 4-2: Overview of experiments at the MBR pilot plant (A) in Darmstadt-Eberstadt.

Purpose of sub-experiment	Feed	Day of operation	Operational parameters
Influence of sludge characteristics and operating conditions on membrane fouling	Municipal wastewater	0-723	See *Table 4-3*
Impact of a salt brine solution on membrane performance		605-723	

The following experiments were conducted at the MBR pilot plant (A):

- Investigation of the influence of sludge characteristics on membrane fouling

In order to investigate the influence of sludge characteristics on membrane fouling, experiments with different sludge ages between 10 and 35 days were carried out. The period of each sludge age test lasted at least 3 times the respective sludge age. To determine the fouling potential, the permeability was continuously evaluated by measuring both TMP and permeate flow. To assess the sludge condition in each testing phase of the respective sludge age, the following parameters were determined: CST, COD, MLSS, proteins, polysaccharides. In addition, viscosity measurements were conducted and microscopic images were prepared at regular intervals.

- Investigation of the impact of backwash, using a salt brine solution, on membrane performance

The investigation of membrane backwash with a salt brine solution was to provide information on the effect of cleaning clogged membrane pores. The change in electrolyte concentrations via the use of salt brine is meant to remobilize ionogenic macromolecules that clog the membrane pores, allowing the blocked pores to be rinsed free. Following the principle that a salt solution holds free charge carriers that shield the monomer charge weakening electrical interaction, experiments with different concentrations between 1 % and 3 % were conducted.

4.1.1.3. Measuring protocol

During operation, membrane performance was evaluated via chemical analyses of influent and effluent samples and activated sludge characteristics. *Table 4-3* depicts the measuring program with its analysis parameters.

Table 4-3: Analysis parameters and measuring program.

Parameter	Interval	Notes
Influent into the MBR tank		
COD [mg O_2/L]	daily	grab sample
$COD_{(0.45\,\mu m)}$ [mg O_2/L]	3 x week	grab sample
NH_4^+-N [mg N/L]	weekly	grab sample
NO_3^--N [mg N/L]	weekly	grab sample
Suspended solids [mg/L]	daily	grab sample
Ignition loss [%]	daily	grab sample
pH value [-]	daily	grab sample
Conductivity [μS/cm]	daily	grab sample
Anionic surfactants [mg/L]	1	grab sample
Proteins, polysaccharides [mg/L]	1	grab sample
MBR tank		
MLSS [g/L]	daily	grab sample
Ignition loss [%]	daily	grab sample
CST [s]	daily	grab sample
pH value [-]	daily	grab sample
Conductivity [μS/cm]	daily	grab sample
$COD_{(0.45\,\mu m)}$ [mg O_2/L]	daily	grab sample
Viscosity[1] [mPa·s]	[1]	grab sample
Proteins, polysaccharides [mg/L]	[1]	grab sample
Microscopic image	[1]	grab sample
Effluent		
COD [mg O_2/L]	daily	grab sample
NH_4^+-N [mg N/L]	weekly	grab sample
NO_3^--N [mg N/L]	weekly	grab sample
Turbidity [NTU]	daily	grab sample
pH value [-]	daily	grab sample
Conductivity [μS/cm]	daily	grab sample
Proteins, polysaccharides [mg/L]	[1]	grab sample

(1) – Analyses were conducted irregularly.

4.1.2. MBR pilot plant (B) in Wiesbaden-Biebrich

4.1.2.1. Plant set-up

Figure 4-2 shows the design of the MBR pilot plant (B) on the site of Microdyn-Nadir in Wiesbaden-Biebrich and the flow sheets for two test phases.

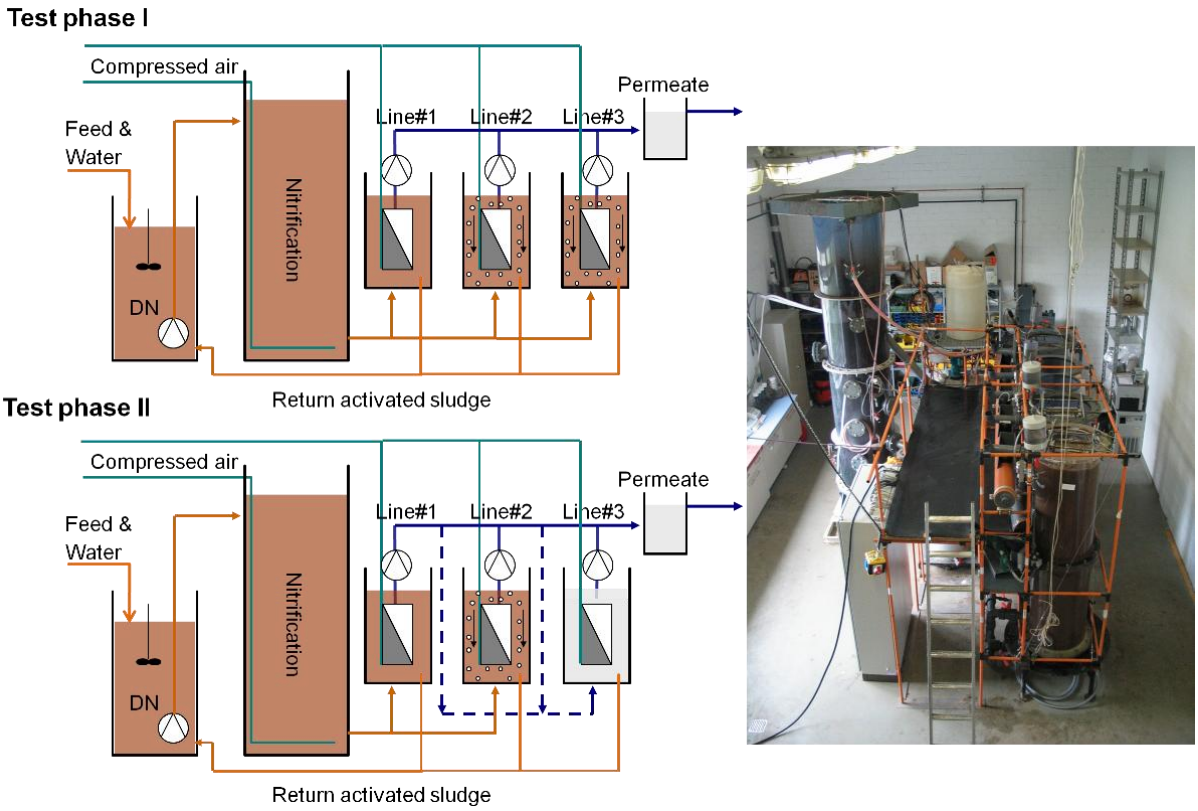


Figure 4-2: Flow sheet (two test phases) and illustration of the MBR plant (B) in Wiesbaden-Biebrich.

The plant, with a total volume of 3.0 m^3, consists of a nitrification reactor (1.2 m^3) and a denitrification tank (0.8 m^3) followed by three parallel running membrane filtration tanks (each 0.33 m^3). The design of this MBR plant only allowed the application of synthetic wastewater (see *chapter 6*) to be inoculated with activated sludge from a MBR plant of Microdyn-Nadir in Wiesbaden-Biebrich. Thereby, the plant was operated under defined conditions so that influencing factors could be determined independently of the feed.

Polyethersulphone (PES) flat-sheet membranes (Bio-Cel® BC 10-10) of Microdyn-Nadir, Germany, with a MWCO of 150 kDa (corresponding to nominal pore size of approx. 0.04 μm) and an active membrane area of 10 m^2 (each) were submerged in the filtration tanks. The operation sequence included forward filtration (510 s), relaxation (30 s), backwash (30s), and relaxation (30 s). Each membrane tank was equipped with a fine-bubble crossflow aeration system. The specific aeration demand per membrane area (SAD_m) was about 0.7 $m^3/(m^2 \cdot h)$. The MBR pilot plant was fully automated and ran parallel in three filtration tanks.

The pilot plant is equipped with the following online measurements: Oxygen concentration, air flow volume (each filtration line and nitrification reactor), flow rate measurement and TMP (each filtration line), pH value, temperature, MLSS concentration (nitrification reactor), and turbidity measurements in the effluent of the filtration line#2 holding granular material (test phase II).

Test phase I

Preliminary tests with activated sludge were carried out in order to test selected granular material (see *Figure 4-2*):

- Line#1 – served as reference for line#2 and line#3; here, the standard MBR operation process without granular material was simulated, applying a MLSS concentration of 4 g/L ± 1.9.
- Line#2 and line 3 were operated parallel, both applying the same MLSS concentration as line#1, however additionally with two different granular materials (see *Table 4-6*) at concentrations of 5 kg/m^3 between the 1st and the 34th day of operation and then 4 kg/m^3 from the 35th day.

Test phase II

In the next step, each filtration tank was operated differently:

- Line#1 – served as reference for line#2 and line#3; here, the standard MBR operation process without granular material was simulated.
- Line#2 – was operated with granular material (see *Table 4-6*) at a concentration of 4 kg/m^3. The abrasive material was retained in the tank by using a screen.
- Line#3 – was operated without granulate in sequence to line#1 and/or line#2. This means, the effluent of line#1 and/or line#2 bearing only soluble compounds < 0.04 μm served as influent for line#3 (see *chapter 4.1.2.2*).

Line#1 and line#2 were operated in parallel at the same MLSS concentration of about 10 g/L whereas line#3 was operated only with permeate (see *chapter 4.1.2.2*).

The effect of changed milieu conditions was tested in line#3 between the 297th and the 398th day. For this purpose, line#3 was operated in parallel to line#1 at the same MLSS concentration of about 10 g/L.

4.1.2.2. Experimental schedule

Table 4-4 gives an overview of experiments conducted at the MBR plant (B) in Wiesbaden-Biebrich. The tests with granulate were carried out over the test period of 45 days (test phase I) and 622 days (test phase II). Between the 148th and the 294th day, the investigation on the impact of truly soluble compounds on membrane fouling was conducted. The effect of changed milieu conditions on membrane fouling was investigated between the 297th and the 398th day.

Table 4-4: Overview of experiments at the MBR plant (B) in Wiesbaden-Biebrich.

Test phase	Purpose of sub-experiment	Feed	Line in operation	Day of operation	Operational parameters
I	Application of granular material	Synthetic wastewater	#1, #2, #3	0-45	COD, MLSS TMP, flux, O_2 temperature SEMs, rejection
II			#1, #2	0-622	COD, MLSS TMP, flux, O_2 temperature turbidity, CST SEMs, rejection
	Research on permeability loss ("truly soluble" matter)	Synthetic wastewater	#1	148-218	COD, MLSS TMP, flux, O_2 temperature turbidity, CST LC-OCD
		Effluent of line#1	#3		
		Synthetic wastewater	#1, #2	219-294	
		Effluent of line#1 (until 260th day); Effluent of line#1 and #2 (261st - 294th)	#3		
	Research on fouling reduction (milieu change)	Synthetic wastewater	#1, #3	297-398	COD, MLSS TMP, flux, O_2 temperature turbidity, CST LC-OCD

The following experiments were conducted:

- Application of mechanical cleaning with granular material in order to minimize the formation of fouling layers

The mechanical cleaning process with granular material was performed in a loop reactor (see *Figure 4-3*). The granulates introduced into the activated sludge filtration tank flow upward alongside the membrane, forced by the crossflow air, and are returned with the downstream water flow outside the plate module, thereby continuously removing the cake layer.

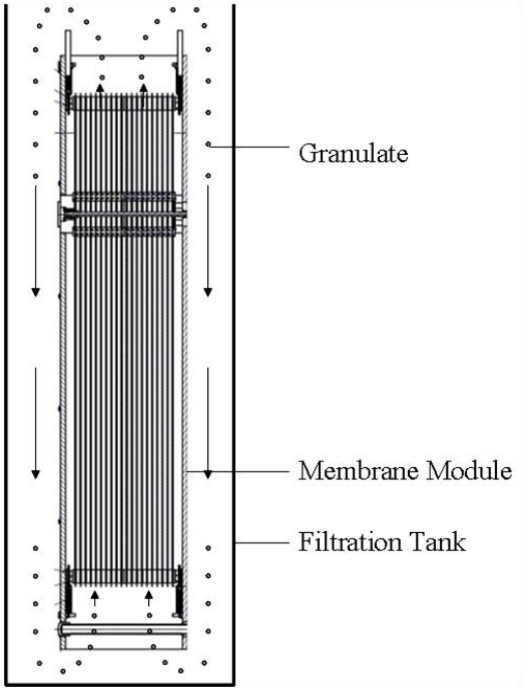


Figure 4-3: Loop reactor with granulate circulation.

Granulate selection

According to *Klegraf (2006)* who investigated expended clay in MBR pilot tests (see *chapter 2.6.2.4*), the material should be non-porous, thus excluding expanded clay as its density changes during operation by taking up water thus forcing the clay to settle. As the granulate should move freely with the liquid flow in the reactor, material density should be > 1 kg/L. Furthermore, as the gap between two membrane sheets is 8 mm, accordingly the diameter of the particles should be < 5 mm. The form of the granulate should be either globular or oval without edges in order to prevent the damage of membrane material. Additionally, the material should be biologically inert.

Particles made from plastics meet all these requirements. Seven different plastic materials were preselected and clean water tests were performed for visual evaluation. Their specifications are given in *Table 4-5*.

Table 4-5: Preselected materials for clean water testing.

Material	Short name	Diameter [mm]	Density [kg/L]
Polypropylene mineral filled	PPTV20	2.5	1.05
Polycarbonate blend	PC	1.5	1.10
Thermoplastic polyurethane elastomer	TPU1185A	3.0	1.12
Polymethyl acrylate	PMMA	2.5	1.18
Thermoplastic polyurethane elastomer	TPU1174D	3.5	1.20
Polybutylene terephthalate	PBT	2.5	1.31
Polyoxymethylene	POM Copo	3.0	1.41

TPU1174D (d = 3.5 mm) and PMMA (d = 2.5 mm) showed the best results in the preliminary clean water tests, both holding densities of about 1.2 kg/L. Therefore, the experiments in activated sludge (test phase I) were performed using these two materials.

However, in test phase II, the lighter polypropylene (PPTV20) granulate (d = 2.5 mm, ρ = 1.05 kg/L) was used, due to excessive settling of the other granulates in test phase I. *Table 4-6* specifies the granulate selected for tests with activated sludge (both phases).

Table 4-6: Granulate selected for tests with activated sludge.

Test phase	Material	Form	Diameter [mm]	Density [kg/L]
1	PMMA	Cylindrical	2.5	1.18
	TPU1174D	Lentiform	3.5	1.20
2	PPTV20	Oval	2.5	1.05

- Determination of the effect of “truly soluble” matter in wastewater and activated sludge on membrane fouling

In order to investigate the effect of "truly soluble" matter (< 0.04 μm) on temporary permeability changes, line#3 was charged with the effluent of upstream line#1 and/or line#2, free of particulate and colloidal matter (see *Figure 4-4*). In this thesis, “truly soluble” matter is operationally defined as material passing the membrane with nominal pore size of approximately 0.04 μm.

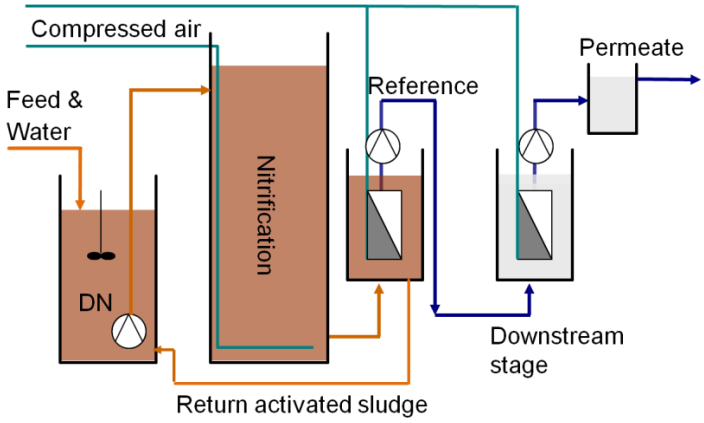


Figure 4-4: Flow sheet of the tests on "truly soluble" matter (< 0.04 µm).

- Investigation of the effect of changed milieu conditions on membrane fouling

From applications of the biofilm process it is well known that a change in milieu conditions, i.e. from aerobic to anaerobic and vice versa, leads to biofilm removal, which in that case is mostly unintentional. In the frame of this thesis, the change in milieu was realized by changing the crossflow aeration system from air to nitrogen in the filtration tank. The change in milieu occurred very fast as a result of high oxygen consumption due to high concentrations of MLSS. The scheme of the discontinuous removal of surface layers by milieu change can be seen in *Figure 4-5*.

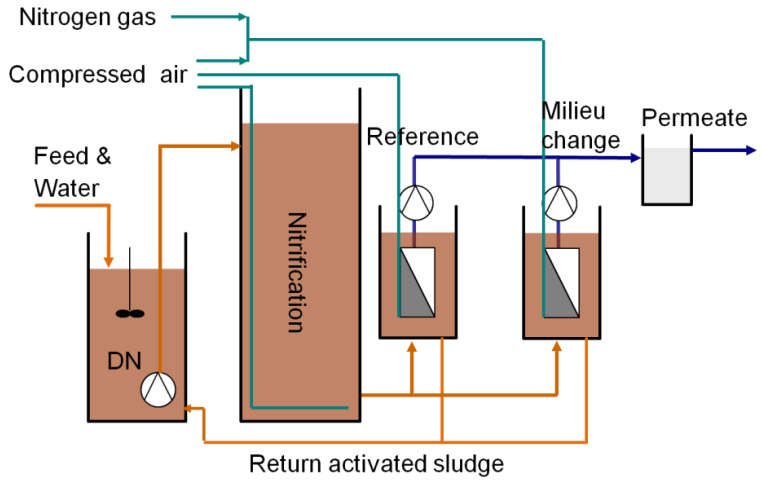


Figure 4-5: Flow sheet of the tests on milieu change.

4.1.2.3. Measuring protocol

Table 4-7 presents the measuring program with its analysis parameters.

Table 4-7: Analysis parameters and measuring program.

Parameter	Interval	Notes
Influent into the MBR tank		
COD [mg O_2/L]	weekly	grab sample
MBR tank		
MLSS [g/L]	daily	grab sample
CST [s]	daily	grab sample
Proteins, polysaccharides [mg/L]	[1]	grab sample
Effluent		
COD [mg O_2/L]	daily	grab sample
Turbidity [NTU]	daily	online
Expertise of membrane material		
SEM-images	[1]	grab sample
Rejection measurements [%]	[1]	grab sample

[1] – Analyses were conducted irregularly.

4.1.3. MBR pilot plant (C) in Wiesbaden-Biebrich

4.1.3.1. Plant set-up

The MBR plant (C) (see *Figure 4-6*) is located at the wastewater treatment plant in Wiesbaden-Biebrich and was charged with mechanically pretreated municipal wastewater. The plant consists of an activated sludge tank with a total volume of 7.8 m^3, in which a membrane module (the same membrane material properties as mentioned above in *Table* 4-1) Bio-Cel® BC 50-50 with an area of 50 m^2 was immersed.

Granulate (ϕ = 3 mm, δ = 1.04 kg/L, polypropylene, globular), with a concentration of 2.6 kg/m^3 was added into the tank and the treated wastewater was sucked in by gravity flow. The granulate

tested here slightly differs (color, shape, diameter) from the previous applied PPTV20 at plant B as the product is not produced or supplied anymore.

The operation mode consisted of permanent filtration without backwash and relaxation breaks. The pilot plant was equipped with two fine-bubble aeration systems: crossflow for fouling control and the standard diffuser on the bottom of the tank for supplying the microorganisms with oxygen. The specific aeration demand (SAD_m) for this membrane module was about 0.8 $m^3/(m^2 \cdot h)$. The pilot plant was started-up with a MLSS content of 4 g/L and during the operation no excess sludge was withdrawn.

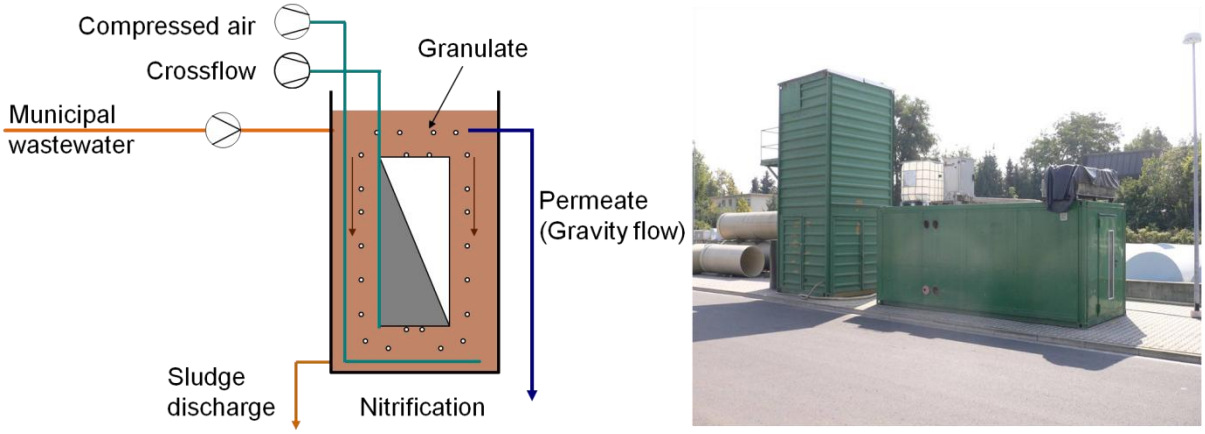


Figure 4-6: Flow sheet and illustration of the MBR plant (C) in Wiesbaden-Biebrich.

For venting the permeate pipe, a manually operated deaeration vessel was installed. In addition, the plant was equipped with an automatically operated excess sludge solenoid valve. The integrated PLC enabled the MBR plant to be operated fully automatically, however, if required, the plant could also be operated manually. Data continuously measured during the operation (TMP, permeate flow and liquid level in the MBR tank, etc.) was stored on a computer via an integrated programmable logic controller.

4.1.3.2. Experimental schedule

Similarly to the MBR plant (B), the application of mechanical cleaning with granular material in order to minimize the formation of fouling layers was tested at the MBR plant (C). The principle of the mechanical cleaning has already been described in *chapter 4.1.2.2*. The only difference is the operation with municipal wastewater instead of synthetic.

4.1.3.3. Measuring protocol

In *Table 4-8*, the measuring program with its analysis parameters is shown.

Table 4-8: Analysis parameters and measuring program.

Parameter	Interval	Notes
Influent into the MBR tank		
COD [mg O_2/L]	[1]	grab sample
MBR tank		
MLSS [g/L]	[1]	grab sample
CST [s]	[1]	grab sample
Temperature [°C]	daily	grab sample
Effluent		
COD [mg O_2/L]	[1]	grab sample
Turbidity [NTU]	[1]	grab sample
Expertise of membrane material		
Rejection measurements [%]	[1]	grab sample

[1] – Analyses were conducted irregularly.

4.1.4. Pilot plant (D) - glass basin (TU Darmstadt)

4.1.4.1. Plant set-up

The tests on the hydraulic optimization of the crossflow aeration system with regard to the energy demand were conducted in clean water in a glass basin at the TU Darmstadt. The construction of the tank allowed precise observation of rising air bubbles and the fluid flow. Dimensions of the basin are as follows: 3.0 m length, 1.5 m width, and 4.0 m depth (see *Figure 4-7* left). To realize the tests, the basin volume was reduced to 3 m^3 by retrofitting a baffle. Dimensions of the reduced volume are 1.5 m length, 1.0 m width, and 2.0 m depth (see *Figure 4-7* right). The membrane module was placed in the middle of the basin. The basin was filled with clean water which was replaced after each experiment. Flat-sheet membranes (Bio-Cel® BC 100-100) of Microdyn-Nadir, Germany, with an area of 100 m^2 were immersed into the basin. The membrane module was equipped in sequence with a coarse-bubble crossflow aeration system and with a fine-bubble crossflow aeration system.

The compressed air was generated by a rotary piston fan (Aerzener Maschinenfabrik GmbH, type GMA 10.0). An adjustable frequency converter allowed continuous control of the air volume. For precise measurement of air volume rates a lobed impeller flow meter (Aerzener G 65, type ZB 039.0), with a pressure gauge and a thermometer on the pressure side of the fan, was installed. The standard air flow, as intake volume (dry air), was related to the standard pressure of 1.013 hPa and the air temperature of 0 °C.

Figure 4-7: Glass basin (left); selected volume of the glass basin for experiments (right).

The crossflow aeration system has proved to be a powerful tool for boundary layer and fouling control. The air bubbles resulting from high, turbulent flow, are directed rapidly towards the membrane surface in order to minimize membrane fouling and are finally discharged out of system.

- Fine-bubble crossflow aeration system

The fine-bubble crossflow aeration system was placed below the membrane module (see *Figure 4-8* right). The aeration system consists of seven perforated PVC pipes (drilling of 35 x 50 mm; gap of 25 mm) with a diameter of 20 mm, each. The fine-bubble aeration is generated via the air outlet from fine slots (2-3 mm) of EPDM (Ethylene-Propylene-Dien-Monomer) membranes covered on a PVC pipe. The fine-bubble aeration system was installed 0.23 m above the basin bottom. In static conditions, the water level of the basin was 2.0 m, resulting in an immersion depth of 1.77 m.

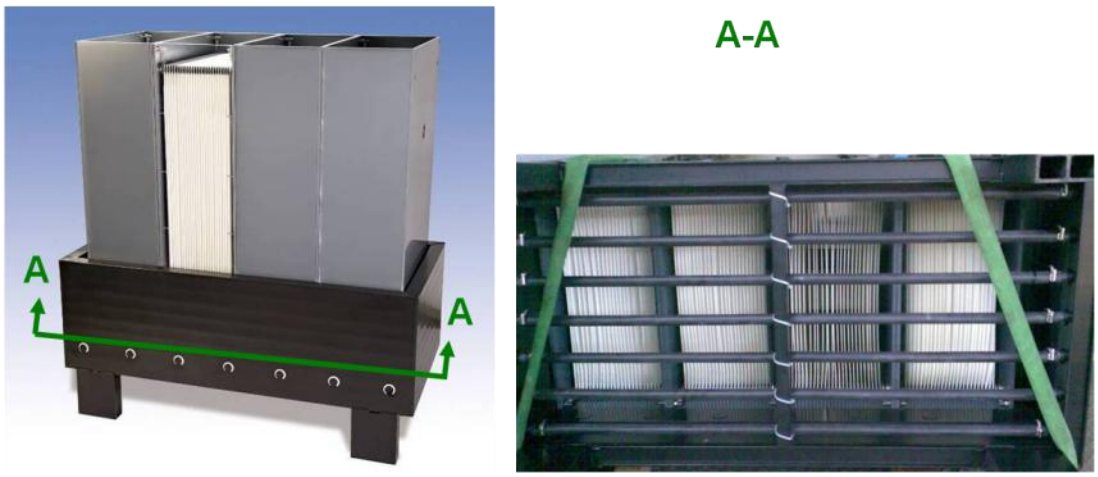


Figure 4-8: Membrane module BC-100 (left); cross-section of the fine-bubble crossflow aeration system (right).

- Coarse-bubble crossflow aeration system

The coarse-bubble crossflow aeration system was arranged below the membrane module (see *Figure 4-9*) and consists of nine perforated PVC pipes (drilling diameter of 1 mm; gap of 5 mm) with a diameter of 20 mm, each. The coarse-bubble aeration system was installed 0.55 m above the basin bottom. In static conditions, the water level of the basin was 2.0 m, resulting in an immersion depth of 1.45 m.

Figure 4-9: Cross-section of the coarse-bubble crossflow aeration system.

4.1.4.2. Experimental schedule

The objective of the glass basin experiments was to optimize the crossflow aeration system with regard to its energy demand its efficiency, both in view of fouling control. In the glass basin, clean water tests on oxygen transfer were performed at different air volume rates (20 m^3/h, 40 m^3/h, 60 m^3/h, and 80 m^3/h).

4.1.4.3. Measuring protocol

In order to classify and evaluate the test results, additional parameters (air volume flow, water temperature, air temperature, water level, back pressure of crossflow aeration systems, and air pressure) were determined.

5. Analyses

5.1. Sampling and conditioning

All results presented in this thesis are based on grab samples, influent, permeate, and activated sludge from the MBR aeration tank. The samples were analyzed within 30 minutes after being taken. Exceptions are measurements that were analyzed externally, e.g. viscosity, LC-OCD (liquid chromatography-organic carbon detection), proteins, and polysaccharides. Prior to dispatch, the samples were cooled and analyzed within two days.

Before analyzing the samples, they were at first homogenized by stirring and shaking. In addition and depending on the analysis, samples were filtered using either a mixed cellulose ester membrane filter (0.45 μm) of Whatman Schleicher & Schuell (soluble/colloidal COD concentration of the influent and activated sludge) or a glass fiber filter GF 92 of Whatman Schleicher & Schuell (suspended solids of the influent, MLSS content of activated sludge). For the filtration of activated sludge samples to be analyzed for proteins and polysaccharides, PES membrane filters 0.45 μm (Pall) were used. The amounts of activated sludge taken for analysis were noted down and considered to calculate the sludge age.

Analyses were carried out in the laboratories of the Institute IWAR, in the laboratory of Mirodyn-Nadir in Wiesbaden-Biebrich, and externally in the laboratory of the Technische Universität Berlin (viscosity measurement, LC-OCD, proteins and polysaccharides concentration).

5.2. Chemical and physical analyses

For analyzing COD in unfiltrated (COD_{inf}) and filtrated ($COD_{0.45\,\mu m}$) samples of the influent, ready-to-use cuvette tests LCK 114 (measuring range: 150-1,000 mg O_2/L) and LCK 314 (measuring range: 15-150 mg O_2/L) of Hach-Lange, Germany, were used. The COD of permeate (COD_{eff}) was analyzed with LCK 314, see above. The detection was via a photometer (DR 2800) of Hach Lange, Germany.

Nitrogen compounds in the influent and effluent of the MBR pilot plant were also measured photometrically. The ready-to-use cuvettes LCK 303 (2-47 mg NH_4-N/L), LCK 304 (0.015-2.0 mg NH_4-N/L), LCK 339 (0.23-13.50 mg NO_3-N/L) und LCK 340 (5-35 mg NO_3-N/L) of Hach-Lange, Germany, were used.

5.3. Characteristics of activated sludge

5.3.1. MLSS, MLVSS

The MLSS and the organic fraction of activated sludge (MLVSS, VSS), i.e. mixed liquor volatile suspended solids, were analyzed according to Standard Methods (*APHA, 1998*). The suspended solids (SS) in the influent were measured according to *DIN 38 409 part 2 (1987)*. The samples were dried at 105 °C (MLSS), ignited at 550 °C (MLVSS) in an oven, and then weighed. The analysis was performed with a sample volume of 100 ml. Volatile suspended solids (VSS), i.e. loss on ignition, means organic matter in the MLSS.

5.3.2. Viscosity and rheological behavior

The rheological examination of activated sludge from the MBR aeration tank was carried out using a rheometer Physica MCR 30 of Anton Paar (Chair of Food Rheology, Technische Universität Berlin). Measurements were performed in the double-gap cylinder measuring system (gap: 40 mm) as duplicates, always at the temperature of 20 °C. Samples were analyzed in a shear rate range of 0 – 1000 s^{-1}.

5.3.3. Microscopic images

The microscopic image of activated sludge was performed weekly with a light microscope of Will (Wetzlar) BX 300 at a 400 times total magnification. The microorganisms in activated sludge were detected by a high-resolution camera and then evaluated.

5.3.4. Filterability (CST)

The CST tests were performed via a capillary suction time filterability tester model 200 (Triton Electronics Ltd, Essex, England). Whatman No. 17 filter paper was used as suction medium.

5.3.5. Coagulation/flocculation (jar test)

Coagulation and flocculation studies were carried out using common jar test equipment, a reliable method to determine the adequate chemicals dosage and to remove turbidity and non-biodegradable colloid/organic matter from the sludge liquor phase. Different dosages of coagulants, e.g. PAX XL9 (polyaluminum chloride), PIX 113 (iron sulfate III), and PIX 111 (iron chloride III) were tested.

The sludge sample was diluted 1:1 with water. The first step of the jar test involved the addition of coagulant to activated sludge and rapid mixing of the sample (as it would be mixed in the flash mix chamber) to completely dissolve the coagulant. Then, the sample was mixed more slowly for a longer period of time, mimicking the conditions in the flocculation basin, and allowing the forming floc particles to cluster together. Next, the mixer was stopped and the flocs were allowed to settle, as would happen in the sedimentation basin. Finally, the sample was filtered through a PES membrane filter and turbidity, COD, and DOC analyses were performed.

5.3.6. Fractionation experiments

Activated sludge from the MBR plant (A) in Darmstadt-Eberstadt was fractionated into four groups: 0.2-0.45 μm, 0.1-0.2 μm, 0.04-0.1 μm, and $< 0.04\,\mu$m. First, the free water was separated from the sludge by sedimentation and/or centrifugation, respectively. Subsequently, the resulting water sample was filtered using three different PES membrane filters (Pall) with pore sizes of 0.45 μm, 0.2 μm, and 0.1 μm, respectively. As the PES flat-sheet membrane of Microdyn-Nadir, Germany, has a nominal pore size of approx. 0.04 μm, the effluent of the MBR plant comprised the fraction $< 0.04\,\mu$m. COD and DOC analyses were performed for each fraction.

5.4. Characteristics of activated sludge supernatant

5.4.1. Soluble/colloidal matter

The analysis of soluble/colloidal proteins and polysaccharides in the liquid phase of activated sludge and in permeate was determined externally, in the laboratory of the Technische Universität Berlin (Chair of Water Quality Control).

5.4.1.1. Photometric analysis (proteins, polysaccharides)

Photometric analysis was used to quantify proteins and polysaccharides. The calibration of the protein analysis was carried out using bovine serum albumin (BSA) following *Frolund et al. (1996)*, a modified method according to *Lowry et al. (1951)*, while glucose according to *Dubois et al. (1956)* was used for the calibration of the polysaccharide analysis.

For analyzing proteins and polysaccharides, sludge liquor samples were used, gained by centrifugation of activated sludge samples and filtration of the sludge liquor using a PES membrane filter of Pall (0.45 μm).

5.4.1.2. Chromatographic analysis (LC-OCD) - size exclusion chromatography

The LC-OCD analyses with UV (ultraviolet) and online organic carbon detection (manufacturer DOC-Labor Dr. Huber Karlsruhe, Germany) were performed by the Water Quality Control Laboratory of the Technische Universität Berlin.

The size exclusion chromatography system includes a separating column (HW 55 S, GROM Analytik+ HPLC GmbH, Herrenberg, Germany) for separating soluble organic compounds according to their molecular weight. In this column, compounds with large molecular weight elute before the smaller ones do. The separated compounds are detected by UV adsorption at 254 nm followed by organic carbon detection.

The result of an LC-OCD analysis is a chromatogram (see *Appendix B.3*) with more or less distinctive peaks for the detected organic fractions. To quantify the results, the areas below the peaks are integrated and converted into concentrations using a calibration curve. The first biopolymer peak at the organic carbon detector (polysaccharides, proteins, and organic colloids) appears after a retention time of 35 to 55 min, followed by humic substances, building blocks, organic acids, and amphiphilic and neutral substances. The UV chromatograms show a similar distribution, except that polysaccharides are not detectable by UV as they have no double bounds necessary for the absorption of light with a wavelength of 254 nm. All samples were diluted 1:5.

To separate the particulate matter from the soluble phase, a sludge sample was centrifuged and then filtrated using a 0.45 μm filter (supor200, PES, Pall GmbH). The selected filters had been tested in preliminary investigations. It was found out that neither polysaccharides nor proteins are adsorbed on the filter or released into the solution.

5.5. Membrane material testing

Some membrane samples were cut out for rejection measurements and SEM images in order to examine membrane material for any damage caused due to the operation with granular material.

5.5.1. Scanning electron microscopy (SEM)

The membrane surfaces were examined via a SEM along with computerized image analysis. Both faces (sheets A and B) of the membrane (see *Figure 5-1*) were studied in both test phases at the MBR plant (B) in order to check for possible membrane damage after using granulate. To carry out the analysis, a tenth part of a membrane sheet situated in the middle of the respective module was removed and rinsed. This analysis was not performed for the MBR plant (C) in Wiesbaden-Biebrich.

Membrane samples were evaluated using a microscope of LEO, type Gemini 982, at an accelerating voltage of 5 kV and 20 kV and a pressure of 3 x 10^{-9} mbar. SEM images were taken at a magnification factor of 500 and 1000. The membrane samples (1 cm^2) were coated with an ultrathin platinum coating in order to avoid the accumulation of static electric charge on the test object during the measurement. After that, the samples were prepared for viewing with a scanning electron microscope.

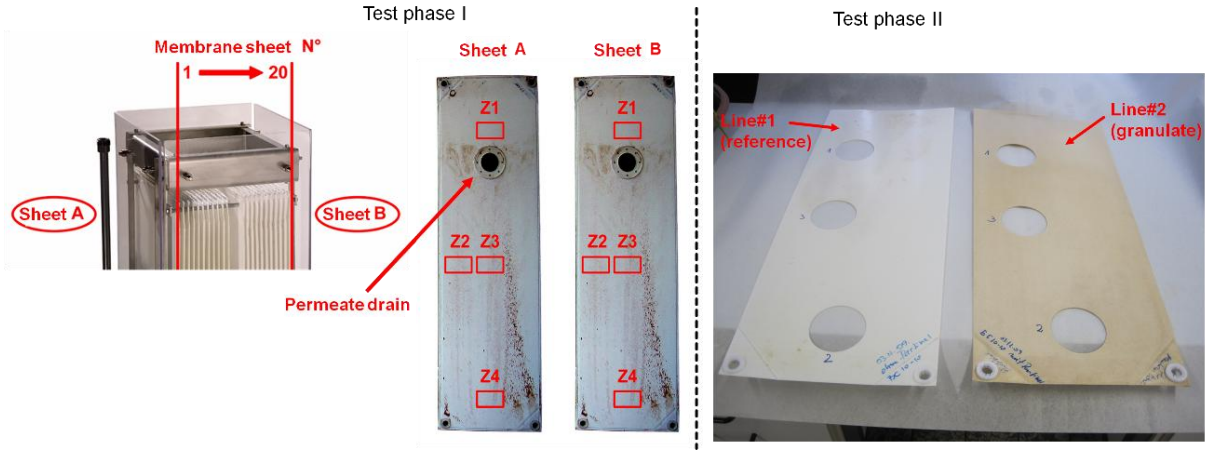


Figure 5-1: Schematic representation of collecting samples of both test phases for SEM images (MBR pilot plant (B) in Wiesbaden-Biebrich).

5.5.2. Integrity tests

5.5.2.1. Membrane MWCO determination – rejection measurements

The membrane MWCO was determined using integrity tests with a test solution. To carry out the analysis, a tenth part of a membrane sheet (both faces A and B) situated in the middle of the module was removed. *Figure 5-1* presents collected membrane samples of both test phases of the MBR pilot plant (B) in Wiesbaden-Biebrich.

After completing the test phase of granulate operation under real conditions (MBR pilot plant (C) in Wiesbaden-Biebrich), ten samples of used membranes were investigated.

The experiments were performed in a thin channel module with an effective membrane area of 42 cm^2, adjustable feed flow, 0.7 bar pressure, 20 °C temperature, and 700 U/min (see *Figure 5-2*). In

order to exclude the positive impact of fouling residue on membrane retention, the membrane samples were prepared in a thin channel module using citric acid (2 %) and sodium hypochlorite (100 ppm).

Figure 5-2: Thin channel module for MWCO determination and water microbiology testing.

5.5.2.2. Water microbiology testing (total coliforms, E. coli)

To investigate the rejection of total coliforms and E. coli by membranes, microbiological analyses were carried out by using water quality kits by IDEXX (Colilert 18) QuantiTray 2000 System, Germany. After 25 months of operation with activated sludge, three membrane samples from the MBR plant (B) were collected each of line#1 (reference) and line#2 (operation with granulate); see *Figure 5-3*. Water microbiology tests for the membrane at the pilot plant (C) were not investigated, as this plant had already been decommissioned.

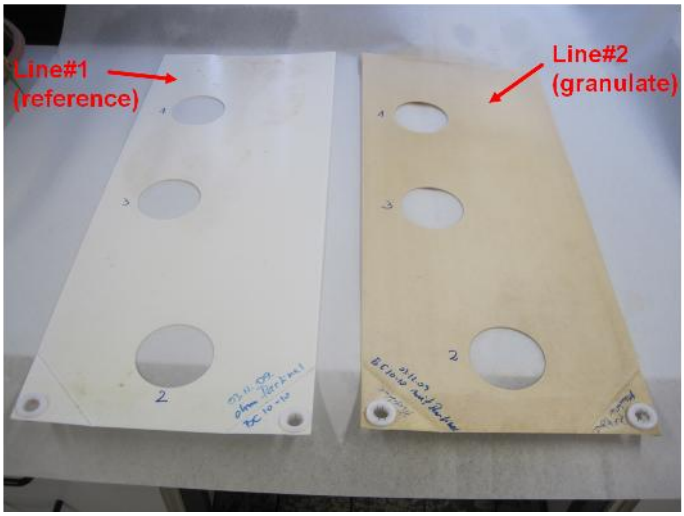


Figure 5-3: Membrane samples (line#1 and line#2) punched for microbiology testing (MBR plant (B) Wiesbaden-Biebrich) after 25 months of operation.

The reference membrane module was placed in chlorinated water (100 ppm Cl) about 5 days prior to collecting samples. Moreover, three samples of a new membrane (UP150T, PES flat sheet) of Microdyn-Nadir were provided as reference for used membrane samples.

Prior to the investigation, 5 liters of activated sludge were collected from a MBR pilot plant of Microdyn-Nadir in Wiesbaden-Biebrich and diluted with 5 liters of drinking water. After mixing, the particulate matter was allowed to settle for 30 minutes. Then, about 3 liters of supernatant (brownish, turbid)

was withdrawn by a suction hose and used for testing. The experiments were performed in a thin channel module with an effective membrane area of 42 cm^2, 0.2 bar pressure, 20 °C temperature, and 300 U/min (see *Figure 5-2*).

The testing included the following steps:

- Each membrane sample was charged with 300 mL supernatant.
- 200 mL of permeate was filtered into sterile bottles (100 mL) under the above mentioned conditions.
- Thereby, the supernatant residue concentrated up to 3 times (further concentration would have been possible).

The accumulation of the supernatant residue in the thin channel module was calculated via *equation 5.1*:

$$c_i \cdot V_i = c_N \cdot V_N$$
$$c_N = c_i \cdot \frac{V_{initial}}{\left(V_{initial} - V_{permeate}\right)} = c_i \cdot N \qquad (5.1)$$

with:
c_i - initial concentration, [mg/L]
c_N - concentration "N" is based on MLSS concentration in the sample, [mg/L]
V_i - initial volume (supernatant), [m^3]
V_N - volume "N" (accumulated supernatant $V_N = V_{initial} - V_{permeate}$), [$m^3$]
N - accumulation factor, [-]

5.6. Turbidity

The turbidity was measured online (WTW VisoTurb 700IQ) in the effluent of line#2 of MBR pilot plant (B) in Wiesbaden-Biebrich and manually (NEPHLA photometer, Dr. Lange) in the MBR pilot plants in Wiesbaden-Biebrich (C) and Darmstadt-Eberstadt (A).

5.7. Brine solution

The brine solution for the membrane backwash was prepared by dissolving sodium chloride (NaCl) in tap water, adjusting the required concentration right before the membrane backwash on site. The final solution was dosed into the permeate tank and the membranes were backwashed at a flow rate of 0.6 m^3/h.

5.8. Oxygen transfer rate

The oxygen transfer rate (kg/h) describes the quantity of oxygen dissolved per hour in clean water (or activated sludge) at 0 mg dissolved oxygen. For the clean water tests, the glass basin (V = 3 m^3)

was filled with tap water. Measurements were performed using the non-stationary absorption method with sodium sulfate according to *DWA (2007b)* to determine the volumetric mass transfer coefficient (k_La). After the dissolved oxygen in the glass basin had been removed by adding sodium sulfate, oxygen (compressed air) was introduced into the basin via a diffuser. During the reoxygenation of the water, the dissolved oxygen concentration was monitored every few seconds until saturation was reached.

The change of dissolved oxygen (DO) in the non-stationary absorption method is described as:

$$\frac{dc}{dt} = k_L a \cdot (c_s - c_x) \tag{5.2}$$

with:
c_s - DO saturation concentration, [mg/L]
c_x - DO concentration, [mg/L]
k_La - apparent volumetric mass transfer coefficient, [1/h]

Figure 5-4 shows the measurement of the oxygen transfer rate using the non-stationary absorption method.

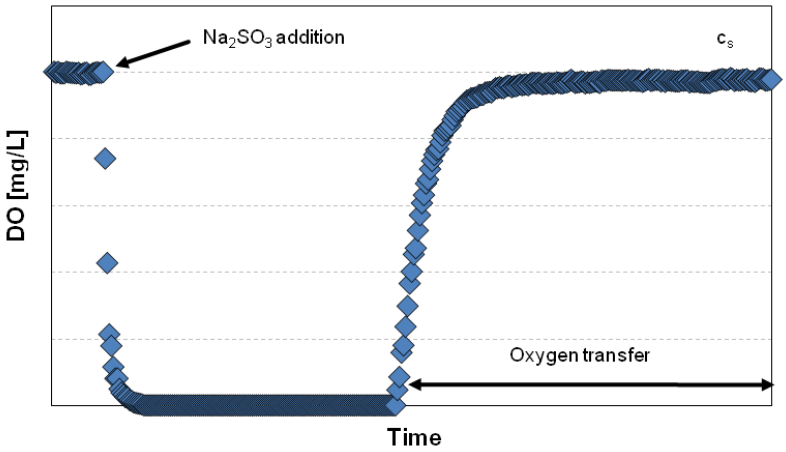


Figure 5-4: Oxygen transfer test using the non-stationary absorption method.

However, increasing the water salinity because of sodium sulfate leads to false results. Therefore, after each test the water had to be renewed. To accelerate the oxidation of sodium sulfate, a catalyst cobalt chloride ($CoCl_2$ x $6H_2O$), technically pure, had previously been added to the clean water. All tests were performed in the course of aeration system operations. Three oxygen sensors of Orbisphere were used, calibrated prior to installation using an oxygen saturation table (*DIN 38 408, part 23*) and considering the current air pressure.

During the tests, oxygen concentrations were continuously measured and recorded automatically. The oxygen transfer capacity in clean water can be calculated by converting the given boundary conditions, such as water temperature, air pressure, tank volume, etc., to standard conditions (20 °C; 1.013 hPa and 0 mg/L oxygen content).

The result of clean water tests are the parameters k_La and c_s. By knowing these parameters, the standard oxygen transfer rate (SOTR) can be calculated.

$$SOTR = \frac{k_L a_{20} \cdot c_{s,20} \cdot V}{1000} \text{ [kg } O_2\text{/h]} \quad (5.3)$$

with:
V - volume of the tank , [m^3]

The specific standard oxygen transfer efficiency (SSOTE) describes the percentage of the mass of oxygen in an injected air stream dissolved into clean water at STP (standard temperature pressure conditions); see *equation 5.4*.

$$SSOTE = \frac{1000 \cdot SOTR}{h_d \cdot Q_f \cdot 0.299} \text{ [%/m]} \quad (5.4)$$

with:
h_d - diffuser depth , [m]
Q_f - air flow rate, [m^3/h]

The aeration efficiency (SAE) can be calculated if the compressor efficiency is known (see *equation 5.5*).

$$SAE = \frac{SOTR}{P} \text{ [kg } O_2\text{/kWh]} \quad (5.5)$$

with:
P - energy demand for oxygen transfer, [Wh/(m^3·m)]

6. Results and discussions

6.1. MBR plant (A) in Darmstadt-Eberstadt

6.1.1. Efficiency of biological wastewater treatment of the MBR plant

6.1.1.1. Composition of municipal wastewater

Table 6-1 represents the influent concentrations of the MBR plant (A) in Darmstadt-Eberstadt over the whole period of investigation. Influent loads increased between the 157th and the 270th day (see *Figure 6-1*) possibly due to discharge of wastewater from a paper mill in the catchment area.

Between the 430st and the 640th day, the influent contained high concentrations of surface active substances (up to 40 mg/L, see *Appendix A.1*), thus reducing the surface tension of the wastewater and consequently providing optimal conditions for foaming and bulking.

Table 6-1: Influent concentrations of the MBR plant (A) being separated in two periods (0-156;271-723[(1)]/157-270[(2)]).

	COD [mg O_2/L]	$COD_{0.45\mu m}$ [mg O_2/L]	NH_4^+-N [mg N/L]	NO_3^--N [mg N/L]	SS [mg/L]	pH [-]	Conductivity [μS/cm]
Number of samples	397/65	219/35	86/14	86/14	375/64	390/64	372/64
Min	90/87	39.4/48	13.1/8.6	0.04/0.65	20/50	7.29/7.5	262/168
Max	1204/1168	492/585	136/99	7.42/1.63	1210/600	9.84/8.55	4070/2410
Average value	536/765	139/321	69.3/61	0.82/0.99	289/348	8.02/8.11	1629/1798
Standard deviation	191.3/253.2	54.5/137.3	28.5/28.8	0.78/0.26	153.6/115	0.32/0.23	531/592

(1) - representation of the measured values over the whole period of investigation except for the period of the increased influent load between the 157th and the 270th day.

(2) - representation of the measured values measured between the 157th and the 270th day.

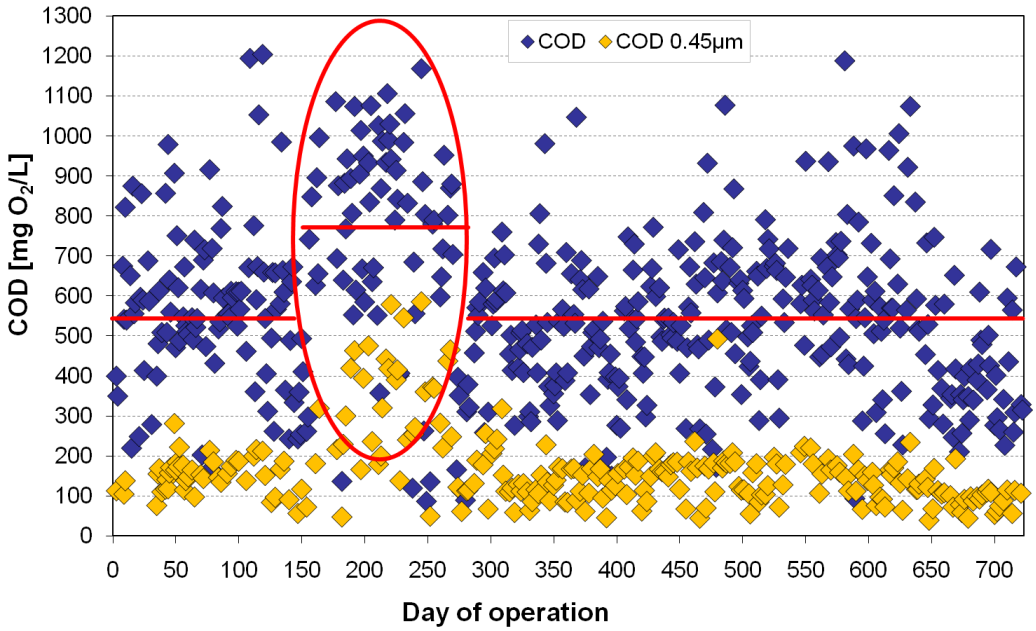


Figure 6-1: Trend of COD and $COD_{0.45µm}$ concentrations in the influent of the MBR plant (A).

6.1.1.2. MLSS and MLVSS

Figure 6-2 shows the trend of MLSS and MLVSS of activated sludge. In the commissioning phase, the MBR plant was inoculated with 1 m^3 of activated sludge from the WWTP Darmstadt-Eberstadt. During the first four weeks after commissioning, there was no sludge wasting and a strong growth of MLSS was observed. Starting at a MLSS concentration of 14 g/L, excess sludge was wasted daily, and the SRT was set at 30 days. Between the 97th and the 114th day, the 233rd and the 255th day, the 229th and the 244th day, the 409th and the 415th day, the 430th and the 557th day, and the 632rd and the 638th day the operation of the MBR plant was not stable due to foaming, bulking and/or technical malfunctioning. These phenomena led to an increased loss of biomass in the system and the decline of the SRT. Due to its poor quality as a result of long-term foaming, ca. 3 m^3 of activated sludge (40 % of the plant) was exchanged against fresh sludge from the WWTP Darmstadt-Eberstadt on the 438th day of operation.

In general, variations in MLSS concentrations resulted from fluctuating influent loads (see *Figure 6-1*) and time lags between sampling, MLSS analyses, and the resulting adjustment of sludge wasting rates.

The term loss on ignition stands for the organic fraction of activated sludge. At the beginning of the operation, loss on ignition was about 75 % and stayed almost constant over three months. Then it increased to > 80 % due to the high loss of biomass associated with a reduction in the SRT. The MBR plant was put out of operation and the aeration tank was completely emptied in order to install a new fine-bubble aeration system on the bottom of the tank (on the 140th day of operation). After restart, the loss on ignition adjusted again to 75 %. Possibly, the fluctuations were caused by the deposition of “inorganic sediment” that was stirred up during tank refilling. Afterwards, the loss on ignition varied between 70 % and 86 %, depending on the SRT adjusted.

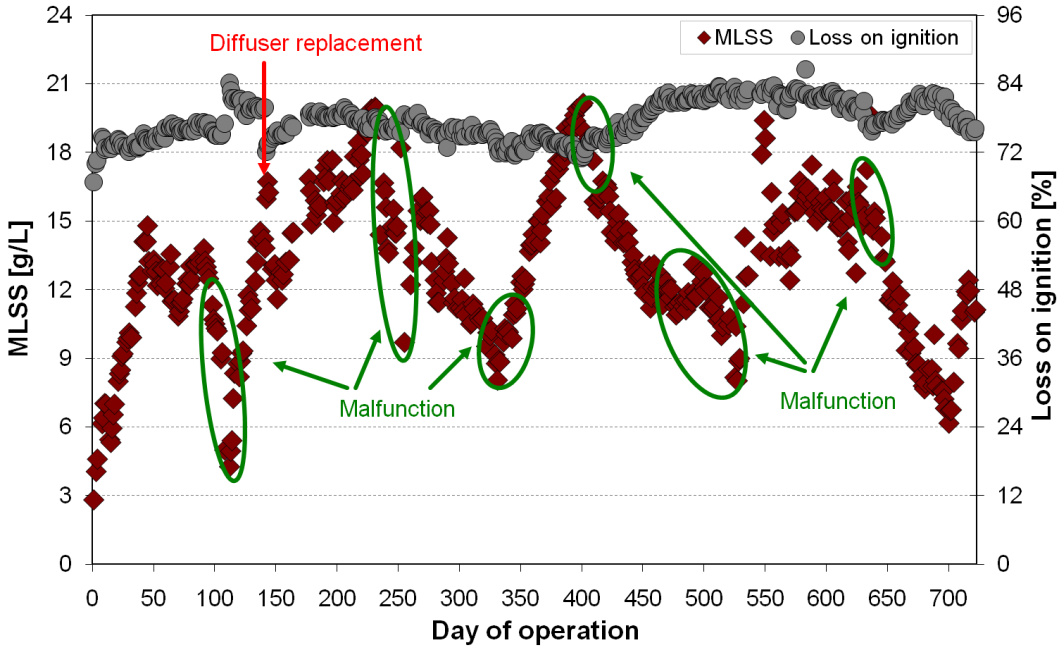


Figure 6-2: Trend of MLSS and loss on ignition in activated sludge over the whole period of investigation.

Activated sludge from municipal wastewater treatment plants with pretreatment shows loss on ignition values between 70–75 %, according to *ATV-Handbuch (1997)*. *Rosenberger (2003)* put together several MBR plants according to the percentage of loss on ignition. The values were in the high range of organic constituents, thereby independent on operating conditions. For MLSS concentrations between 2 and 18 g/L, loss on ignition ranged up to 86 %.

6.1.1.3. Organic sludge loading

Figure 6-3 shows the organic sludge loading rates with corresponding SRTs over the whole period of operation. The organic loading rate (OLR) is based on the COD influent load, calculated from the COD concentration in the influent and the influent flow rate per mass of activated sludge, the latter being calculated from the MLVSS concentration and the volume of the activated sludge tank.

Parallel to the rising concentrations of MLVSS, at first the OLR dropped strongly. Afterwards, the values mostly stayed between 0.02 and 0.2 kg COD/(kg MLVSS·d) with a few outliers depending on SRT, MLSS concentration, and influent load of COD. The considerable fluctuations result from large variations in the wastewater composition at fixed influent flow rates or due to technical malfunctioning during operation.

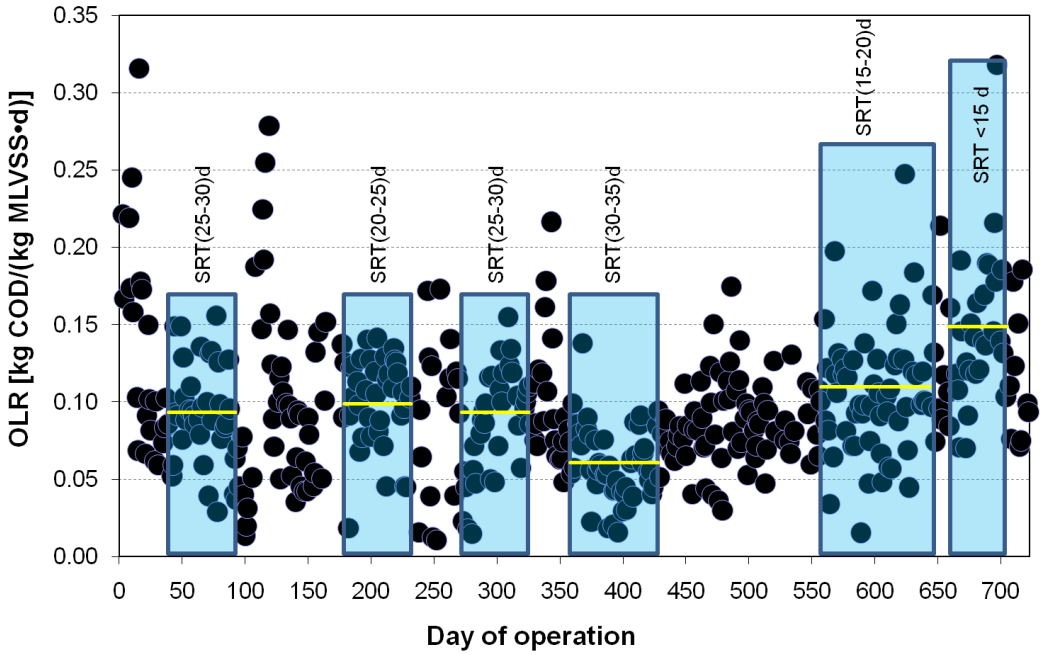


Figure 6-3: Organic loading rate (OLR) and SRTs of the MBR plant over the whole period of investigation.

6.1.1.4. Microscopic image of activated sludge

Microscopic images of activated sludge facilitate the evaluation of the results of physical-chemical analyses. Qualitative and quantitative changes in the microbial community are indicators for disturbances, such as insufficient oxygen supply, process instability, and growth of filamentous microorganisms, and in many cases allow conclusions to be drawn on the causes. The monitoring of microbial community is therefore extremely important.

Return sludge from the municipal WWTP in Darmstadt-Eberstadt was used to inoculate the membrane bioreactor. During the subsequent operation, a constant change in the population structure was observed, on the one hand caused by new species being introduced with raw wastewater, on the other hand as a result of current sludge loading of the plant. During the investigation period with a SRT of between 30 and 35 days (see *Figure 6-3*), rhizopods (amebas) were observed. Amebas are well known as an indicator for high SRT, low sludge loading, complete nitrification, and sufficient oxygen supply. In that phase, a large diversity of microorganisms was observed, however with the dominance of metazoan and worms. *Lemmer (1990)* stated that those metazoans are food competitors particularly for ciliates. Rotifers and worms are frequently identified in old sludge. The microbial community populating activated sludge shows its good properties and the process stability.

After decreasing the SRT to values < 20 days (on the 558th day), initially an enormous growth of ciliates, attached to sludge flocs, was observed. However, over time the attached ciliates were replaced by crawling ciliates. The experimental periods between the 97th and the 114th day, and the 430th and the 557th day were interrupted due to the appearance of filamentous bacteria. Enormous foaming and bulking led to process instability that was reflected in the increased occurrence of attached ciliates. One of the reasons for the dominancy of filamentous microorganisms might be the introduction of paper mill wastewater, creating an atypical composition of the influent wastewater with high concentrations of surfactants.

6.1.1.5. Elimination of organic compounds

The MBR plant (A) was charged with an average inflow of 0.78 m^3/h, controlled by the liquid level in the tank. The daily average influent flow was about 11 m^3/d. The hydraulic retention time in the MBR was 17 hours at an initial tank volume of 7.6 m^3, and later 10 hours at a decreased volume of 4.6 m^3. The raw wastewater showed large variations in the COD concentrations (100 to 1,300 mg/L, (see *Table 6-1*). The increased concentrations in the influent between the 157th and the 270th day, on average 765 ± 253.2 mg/L, were caused by the additional load from a paper mill in the catchment area (see *chapter 6.1.1.1*). During the whole investigation period, advanced wastewater treatment was realized with regard to the COD, thereby achieving an average COD removal of 95 %.

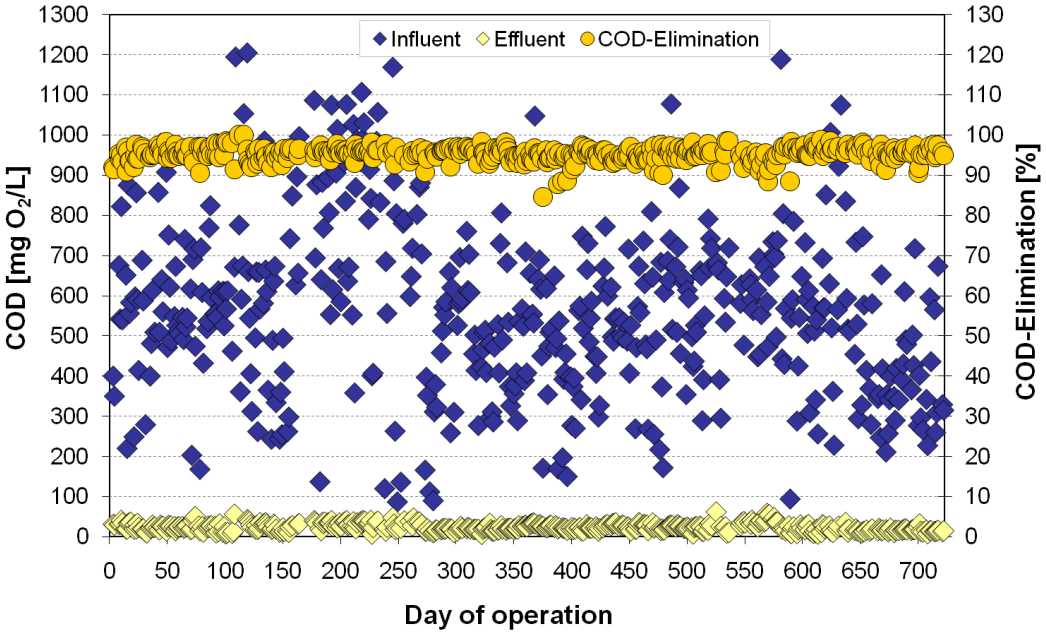


Figure 6-4: Trend of COD elimination and COD concentrations in the influent and effluent of the MBR plant (A).

6.1.1.6. Nitrogen removal

As the MBR (A) plant consisted of only one aerated tank, only nitrification took place without denitrification. Due to the recirculation of supernatant into the influent of the municipal WWTP in Darmstadt-Eberstadt, high ammonium concentrations up to 136 mg/L NH_4^+-N with an average of 68.2 mg/L ± 29, occurred in the influent of the WWTP (see *Figure 6-5*). Nitrate-N concentrations in the influent were 0.9 mg/L ± 0.7 on average. The average NO_3^--N and NH_4^+-N concentrations in the effluent were 42 mg/L ± 25 and 2.5 mg/L with high fluctuations between 0 and 46.5 mg/L, respectively. The nitrification efficiency was 97 % on average over the experimental period, with a few outliers due to malfunction, i.e. foaming and bulking.

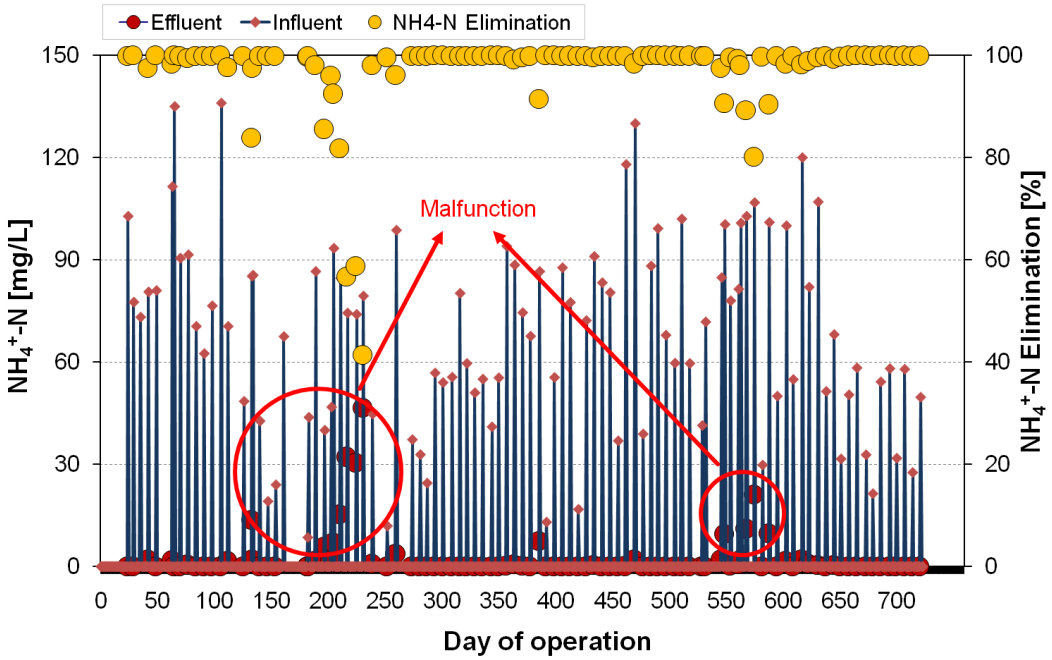


Figure 6-5: Trend of NH_4^+-N elimination and NH_4^+-N concentrations in the influent and effluent of the MBR plant (A).

6.1.2. Efficiency of the membrane filtration process

6.1.2.1. Flux

The flux rates were recorded online by the integrated PLC. In order to determine the course of net and gross flux rates, the daily average values were calculated from the recorded data (see *Figure 6-6*). The gross flux rate is the flux during the filtration time. The net flux rate is thereby defined as the gross flux rate adjusted for production lost during backwash, relaxation, and cleaning. *Figure 6-6* shows that the membrane was operated at 14.5 L/(m^2·h) ± 0.6 gross flux and 10.6 L/(m^2·h) ± 0.6 net flux.

Between the 505th and the 600th day of operation, flux rates slightly dropped to 13 L/(m^2·h) for the gross flux and to 9 L/(m^2·h), excluding some outliers, for the net flux. This deterioration in performance might be caused by the increased TMPs that occurred in this period of time (see *chapter 6.1.2.2*) or due to foaming of activated sludge.

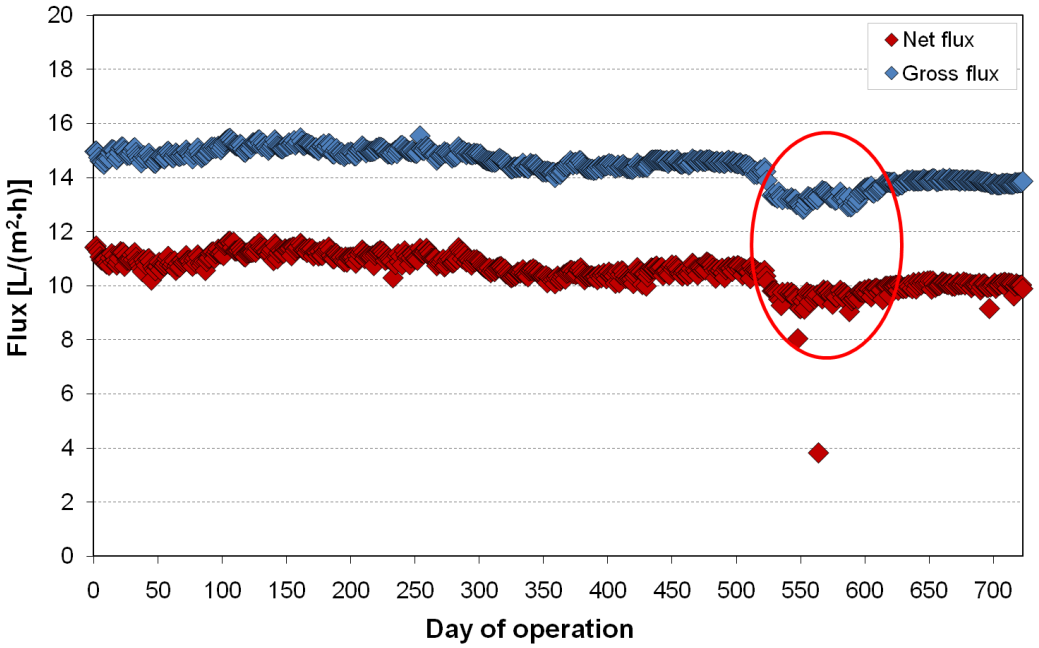


Figure 6-6: Gross and net flux rates over the investigation period at the MBR plant (A).

6.1.2.2. Permeability

In addition to flux, permeability is another key parameter to be used for the assessment of membrane performance. In order to compare hydraulic performance over a long-term operation period, it is necessary to consider the temperature dependency as it affects membrane filtration via changing permeate viscosities. Temperature correction to 20 °C was calculated according to *Judd (2006)*, similar to the k_La (see *equation 2.12*).

Figure 6-7 pictures the trend of the permeability (normalized to 20 °C), temperature, and TMP. The water temperatures in the filtration tank were between 7 °C and 25 °C (16.7 °C ± 4.3 on average). Initially, the membrane module showed a permeability of about 320 L/(m^2·bar·h), which decreased to about 250 L/(m^2·bar·h) within the first two weeks and further to about 180 L/(m^2·bar·h) on the 335th day. On the 345th day, the membrane module was replaced due to failure.

The initial permeability of the new membrane module was only 210 L/(m^2·bar·h), i.e. about 100 L/(m^2·bar·h) lower than the previous module. There is no conclusive explanation for this. Possibly, air was in the membrane pockets. Usual production fluctuations are in the range of 300-450 L/(m^2·bar·h) and thus cannot explain the value of 210 L/(m^2·bar·h). The permeability of the new membrane module decreased right from the beginning. A sharp increase in TMP was observed from the 490th day on, which seems to run parallel to the drop in temperature. Moreover, excessive foaming problems occurred in the period between the 430th and the 557th day of operation. This unstable operation led to declined SRTs due to the biomass loss. The subsequent permeability decline (from the 660th day) might be due to a decrease in SRT below 15 days (see *Figure 6-3* and *Figure 6-19*). Below (*chapter 6.3*), the influencing parameters are discussed in detail.

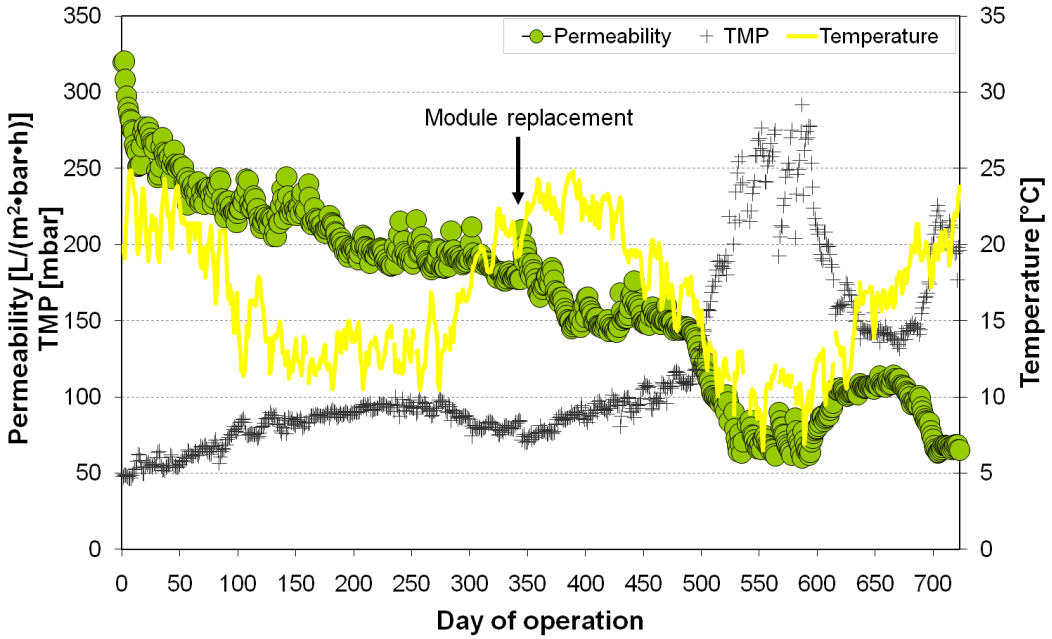


Figure 6-7: Trend of permeability, transmembrane pressure (TMP), and water temperatures. The permeability was normalized to 20 °C.

The TMP increased from 47 mbar up to 100 mbar for the first membrane module and from 70 mbar to 290 mbar for the second module over their respective operating period. During the whole experimental period of 723 days, neither mechanical nor intensive chemical cleaning of membranes was carried out. In order to keep the TMP in the safe range (< 300 mbar), weekly maintenance cleaning using low concentrations of chemicals was performed (see *chapter 6.4.5*).

6.2. MBR pilot plant (B) in Wiesbaden-Biebrich

6.2.1. Efficiency of biological wastewater treatment of the MBR plant

6.2.1.1. Composition of synthetic wastewater

The MBR pilot plant (B) in Wiesbaden-Biebrich was fed with synthetic wastewater that was prepared weekly on-site by dissolving the following chemicals in water (see *Table 6-2*). The concentrated feed continuously flowed into the denitrification tank and was appropriately diluted with tap water.

Table 6-2: Composition of synthetic wastewater of the MBR pilot plant (B) in Wiesbaden-Biebrich.

Chemical	Formula	Concentration [g/L]
Molasses	$C_6H_{12}O_6$	50
Urea	H_2NCONH_2	4.6
Magnesium sulphate	$MgSO_4 \cdot 7H_2O$	4.1
Calcium chloride	$CaCl_2$	0.2
Potassium di-hydrogene phosphate	KH_2PO_4	1.1
Ferric (III)chloride	$FeCl_3$	0.04

6.2.1.2. MLSS and CST

Figure 6-8 shows the course of MLSS and CST in activated sludge of the MBR pilot plant (B). In the commissioning phase, the plant was inoculated with 1 m^3 of activated sludge from the municipal WWTP in Wiesbaden-Biebrich. The first five weeks after commissioning, there was no sludge wasting and a strong growth of MLSS was observed. Starting at a MLSS concentration of 10 g/L, excess sludge was discontinuously wasted and a high SRT in the range of 25-30 days was set. During the remaining course of operation, SRTs stayed between 15 and 30 days (see *chapter 6.2.1.3*).

After about 370 days, changes in sludge characteristics in the MBR plant were observed, in terms of decreasing filterability, increase in CST, and foaming possibly due to a decrease in the F/M ratio (food to microorganisms). Because of a malfunction that resulted in the complete loss of the activated sludge, on the 449th day, the MBR pilot plant was re-inoculated with fresh activated sludge (ca. 0.74 m^3) from a MBR pilot plant of Microdyn-Nadir. Subsequently, the plant was set to the previous operating conditions with a SRT > 25 d. From the 594th day on, problems with foaming led to instable operation. Only after the activated sludge was replaced by and by with fresh sludge, the operation was stable again.

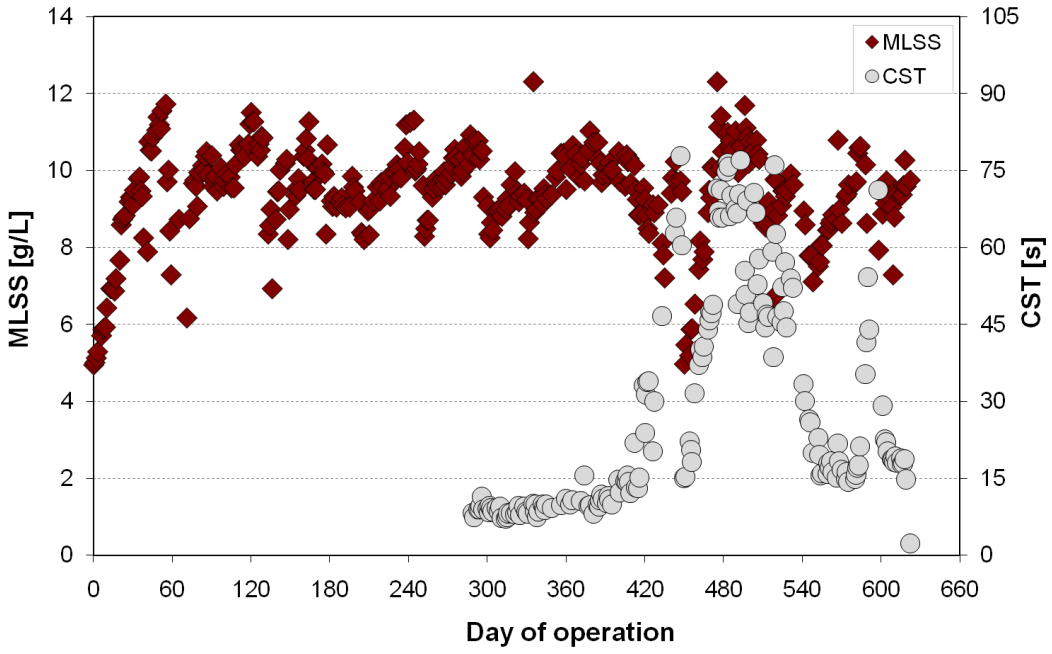


Figure 6-8: Trend of MLSS and capillary suction time (CST) in activated sludge over the whole period of investigation.

6.2.1.3. Sludge loading rate

Figure 6-9 shows the SLR and SRT of the MBR pilot plant (B) during the operation. The SLR is based on the COD influent charges, calculated from the COD concentration in the influent and the influent flow rate per mass of activated sludge, the latter being calculated from the MLSS concentration and the volume of the activated sludge tank. Initially, the SLR decreased strongly, while at the same time the MLSS concentration increased. Afterwards, the values stayed between 0.07 and 0.15 kg COD/(kg MLSS·d). The fluctuations result from several losses of activated sludge and due to occasional fluctuations in the influent flow rate (clogging of a hose). Most of the time, the pilot plant

was operated at high SRTs between 20 and 30 days, and - for only a short period of time - at SRTs in the range of 15 and 20 days.

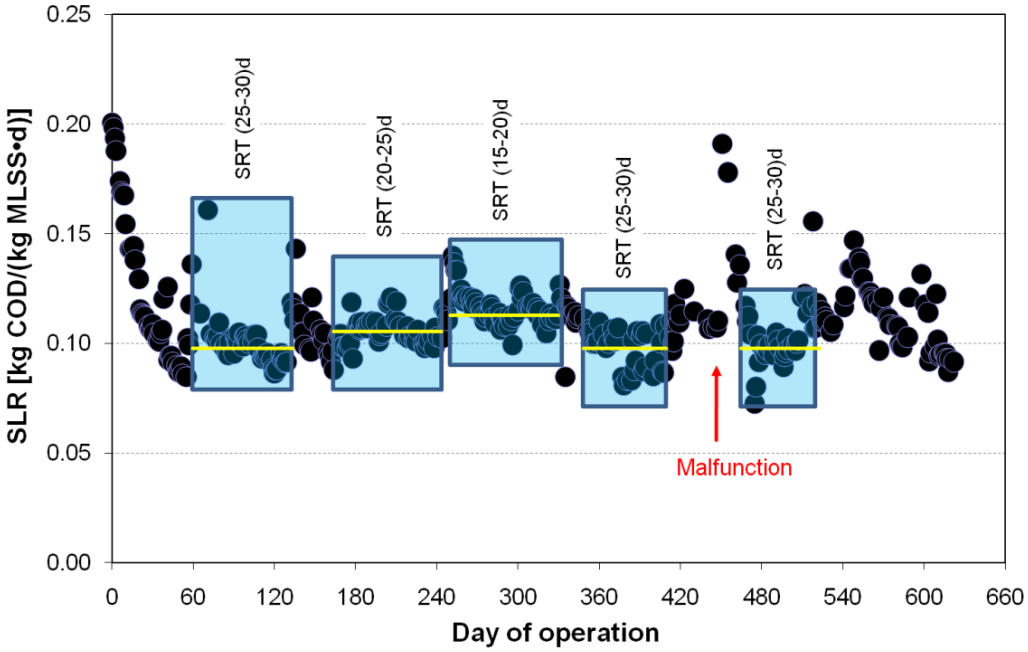


Figure 6-9: Sludge loading rate (SLR) and SRT of the MBR pilot plant (B) over the whole period of investigation.

6.2.1.4. Elimination of organic compounds

The MBR pilot plant (B) consists of three filtration tanks running in parallel. Depending on the experimental phase, a corresponding line was operated at specifically set parameters (see *Table 6-3*). The average daily volume of water was 5.6 ± 0.84 m^3/d, 9.3 ± 1.8 m^3/d, 8.23 ± 3.4 m^3/d, depending on the investigation phase. The relatively high standard deviations results from large variation in the flux rates. The HRT of the activated sludge tank was between 7 and 11.5 hours (V_{BB} = 2.7÷3.0 m^3).

Table 6-3: Operating conditions of the MBR pilot plant (B) over the whole investigation period.

Day of operation	Line in operation	Plant capacity [m^3]	HRT [h]	$COD_{Inf.}$ [mg O_2/L]	$COD_{Eff.}$ [mg O_2/L]	COD-Elimination [%]	Comments
0-147	1, 2	2.7	11.5	486.5±89	29.4±12.5	93.7±2.7	
148-293	1, 2, 3	2.7	6.97	316.5±53	15.3±9.1	95.2±2.7	Line#3 - soluble compounds < 0.04 μm (no activated sludge)
294-622	1, 2, 3	3.0	8.75	330.8±107	11.0±7.1	96.4±3.7	Line#3 – Milieu change (with activated sludge)

The raw water showed large variations in the COD concentrations (200 to 1,000 mg/L) due to faults in a feed dosage (see *Figure 6-10*). During the whole operating period advanced wastewater treatment was realized with regard to the COD, thereby achieving an average COD removal of 95 %.

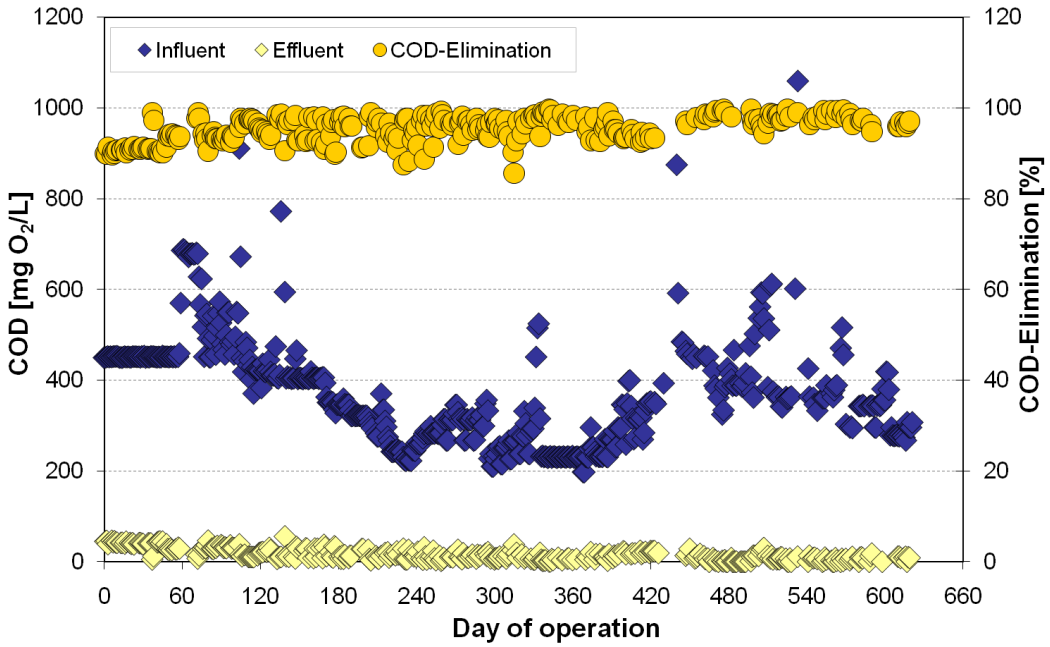


Figure 6-10: Trend of COD elimination and COD concentrations in the influent and effluent of the MBR pilot plant (B).

6.3. Research on permeability loss

The efficiency of the membrane processes basically depends on the interactions between the employed membranes, the activated sludge, and the chosen operating conditions. As the membrane module of Microdyn-Nadir was operated under steady hydrodynamic conditions (flux rate, air flow volume of crossflow system), sludge characteristics (colloidal matter, viscosity, MLSS concentration, CST) could be investigated under different operating conditions (temperature, SRT, composition of influent, etc). An overview of all investigated parameters at the MBR plant (A) in Darmstadt-Eberstadt is depicted in *Figure 6-11*). The parameters are discussed in detail in the following chapter.

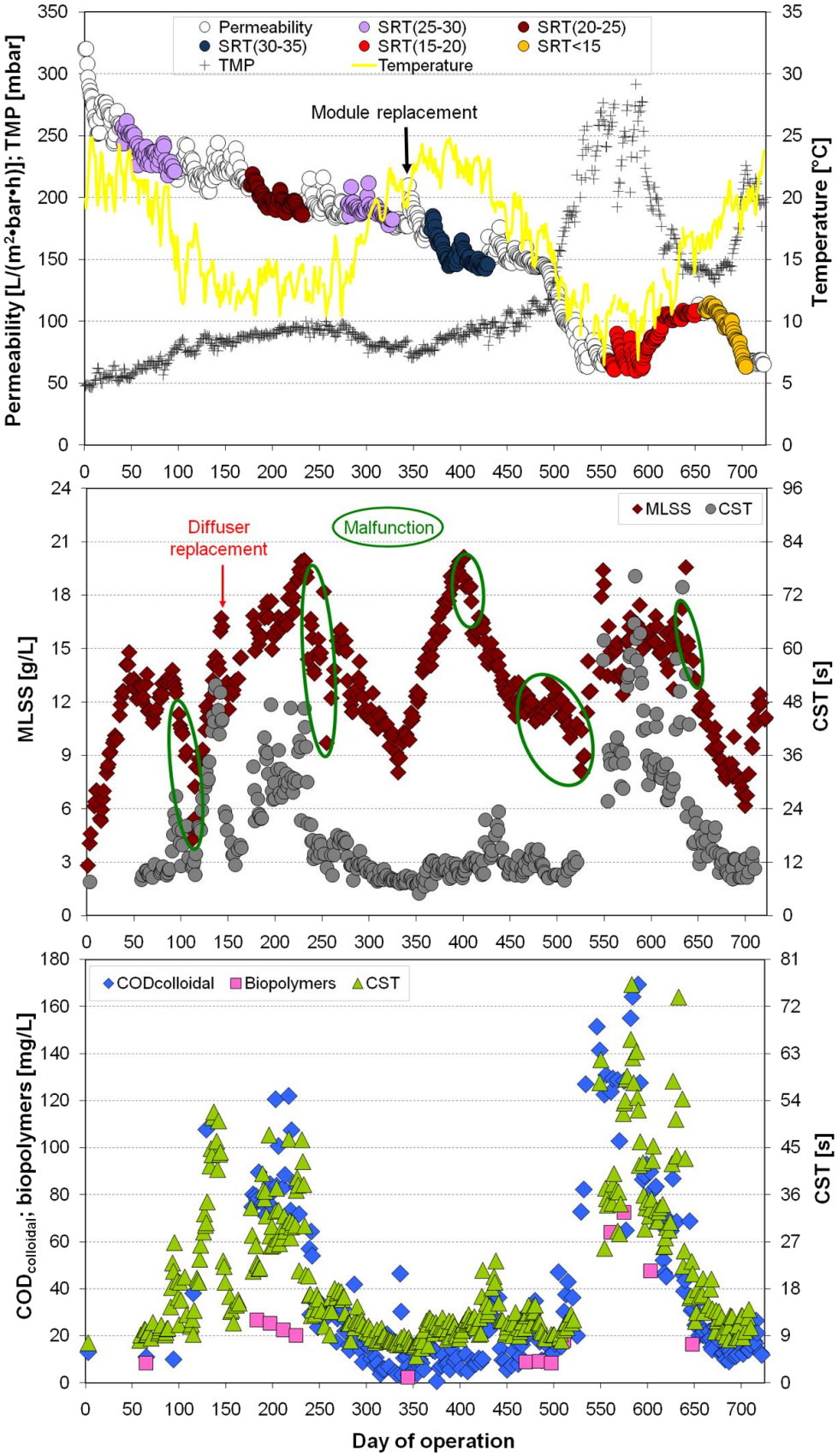


Figure 6-11: Overview of investigated parameters over investigation period.

6.3.1. Influence of activated sludge characteristics on fouling

6.3.1.1. Colloidal matter (proteins, polysaccharides)

Sum parameters, such as COD, proteins, and polysaccharides, are used to quantify the soluble matter in the liquid phase of activated sludge (supernatant). By definition, a fraction of supernatant that passes through a membrane filter of 0.45 μm is considered as "soluble" (*Henze et al., 1999*).

However, with 0.04 μm the pores size of UF membranes is tenfold lower. This means that these membranes can retain colloids that are considered to be soluble according to definition. The difference between $COD_{0.45\,\mu m}$ and $COD_{0.04\,\mu m}$ quantifies the colloidal fraction ($COD_{colloidal}$). In this thesis, particulate matter, colloids, and truly dissolved matter are defined as $> 0.45\,\mu$m, 0.04-0.45 μm, and $< 0.04\,\mu$m, respectively.

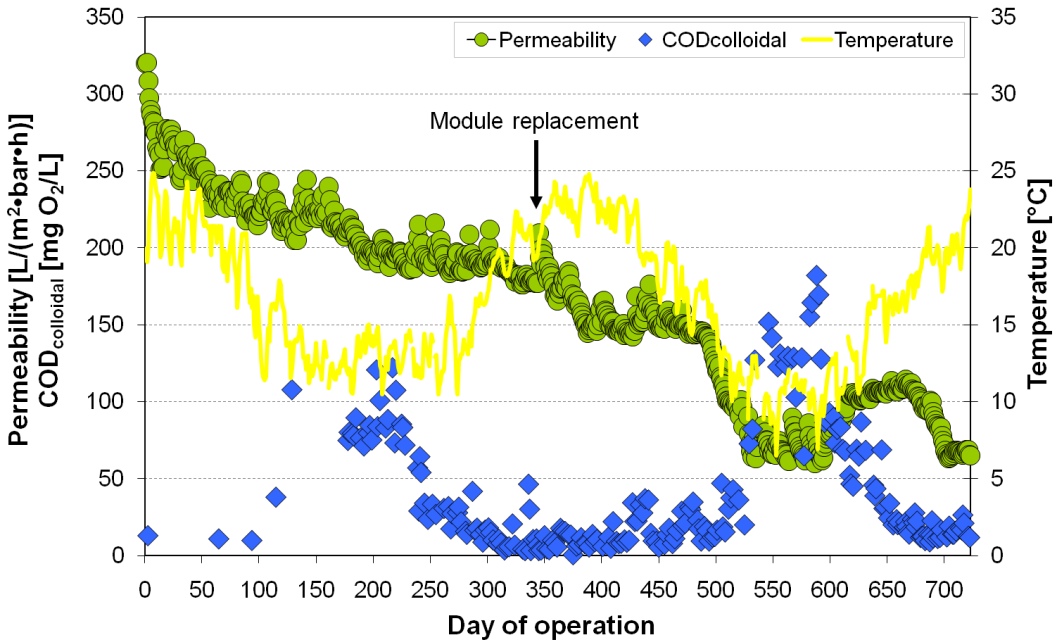


Figure 6-12: Effects of temperature and colloidal COD concentration on fouling behavior.

Figure 6-12 shows the colloidal fraction. A sharp increase in the colloidal fraction was observed between the 115th and the 250th day and again between the 510th and the 640th day of operation. The opposite run of temperature and colloidal fraction may suggest a correlation between these variables.

Temperature is a well-known factor influencing the kinetic parameters of biological processes and plays a significant role during degradation processes and thus in wastewater treatment. Many researchers have already observed the temperature impact on fouling behavior (*Barker et al., 1999, 2000; Jiang et al., 2005; Rosenberger et al., 2006; Drews et al., 2007*).

However, it should be noted that in addition to the temperature other important parameters changed, e.g. SRT (see *Figure 6-19*), and thereby mono-criteria causal connections apparently cannot be deduced in complex systems. Furthermore, it was observed that the combination of low SRTs and low temperature affected the permeability, as the permeability dropped between the 510th and the 540th day. In contrast, the permeability was not negatively affected at high SRTs.

Moreover, due to excessive foaming problems, ca. 3 m^3 of activated sludge had to be replaced against fresh sludge on the 438th day of operation. *Chang and Lee (1998)* state that foaming of activated sludge appears to yield lower membrane permeabilities, attributed to its higher hydrophobicity.

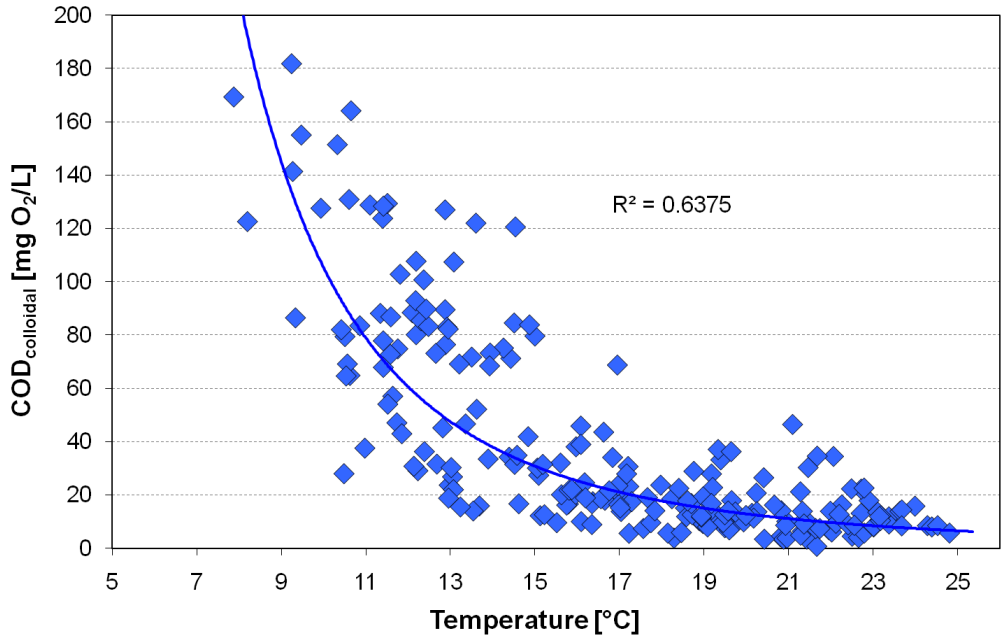


Figure 6-13: Colloidal COD concentration vs. temperature over the whole investigation period.

Although, *Figure 6-13* indicates that temperature directly affects the colloidal COD fraction, further investigations are necessary. In particular, it is important to study to what extent the colloidal fraction contributes to fouling. Whereas a decline in permeability parallel to an increase in the colloidal COD fraction was observed between the 510th and the 640th day, this phenomenon was not observed in the period between the 115th and the 250th day.

Further investigations showed that at high concentrations of the colloidal COD fraction there are also high concentrations of biopolymers (sum of proteins and polysaccharides) in the supernatant (see *Figure 6-14*). On average, the concentrations of proteins and polysaccharides were 19.69 mg/L ± 6.07 and 23.94 mg/L ± 19.92, respectively. The high protein/carbohydrate (P/C) ratios of the supernatant (1.13 ± 0.49) show that proteins were the major soluble supernatant constituent during experiments. This correlation, which is to be investigated further, would have exceeded the framework of this thesis (see *chapter 9*).

Al-Halbouni (2008) reports that higher amounts of EPS, which was related to low SRT or to colder seasons and probably a shift in microbial populations, had a negative impact on sludge properties i.e. filtration index, settling behavior, dewaterability.

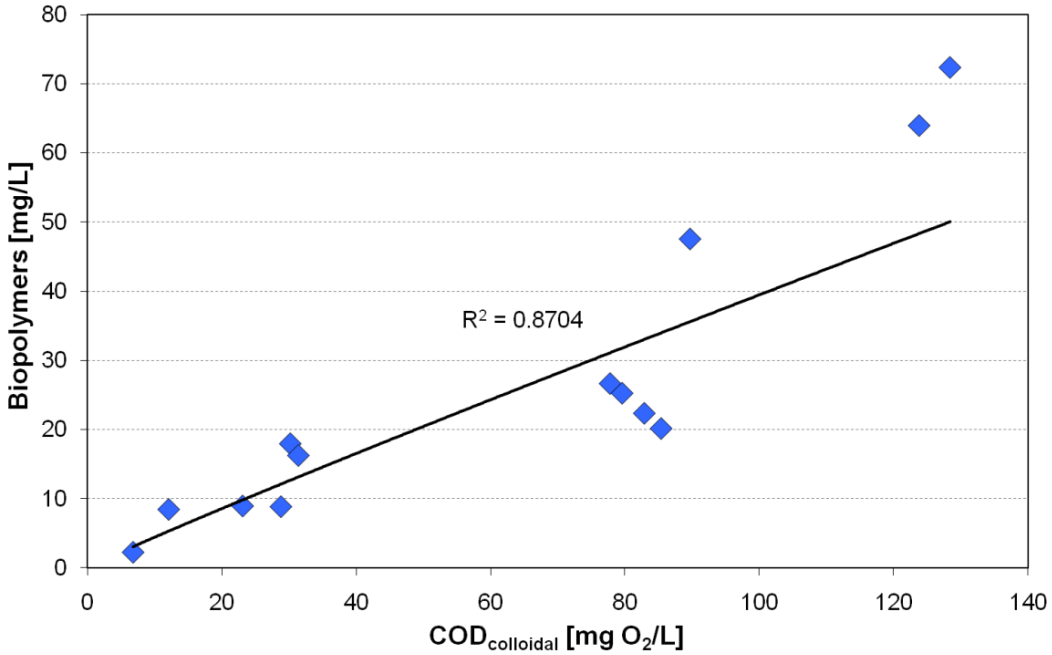


Figure 6-14: Concentration of biopolymers (sum of proteins and polysaccharides) vs. concentration of colloidal COD over the whole investigation period.

Jar tests were performed during periods of high $COD_{colloidal}$ concentrations in the supernatant (winter periods) in order to examine sludge coagulation by adding chemicals and thereby binding colloids and other sludge components in flocs. Three different coagulants were tested and the most appropriate coagulant (polyaluminum chloride - PAX XL9) was chosen for the tests (see *Appendix A.2*). During periods of high $COD_{colloidal}$ concentrations in the supernatant high sludge volume indices (SVI) were observed (see *Appendix A.1*).

Figure 6-15 shows that after adding polyaluminum chloride coagulant the $COD_{colloidal}$ concentration of the supernatant was reduced by up to 80 % of the initial value. The coagulant even bound soluble matter $< 0.04\ \mu m$, as COD concentrations of permeate were slightly higher.

Some authors reported that by adding chemicals (polymers, metal salts, and other substances) biopolymer concentrations (proteins, carbonates) in the supernatant were reduced (*Wett, 2005; Iversen et al., 2006; Yoon and Collins, 2006; Khan, 2008*).

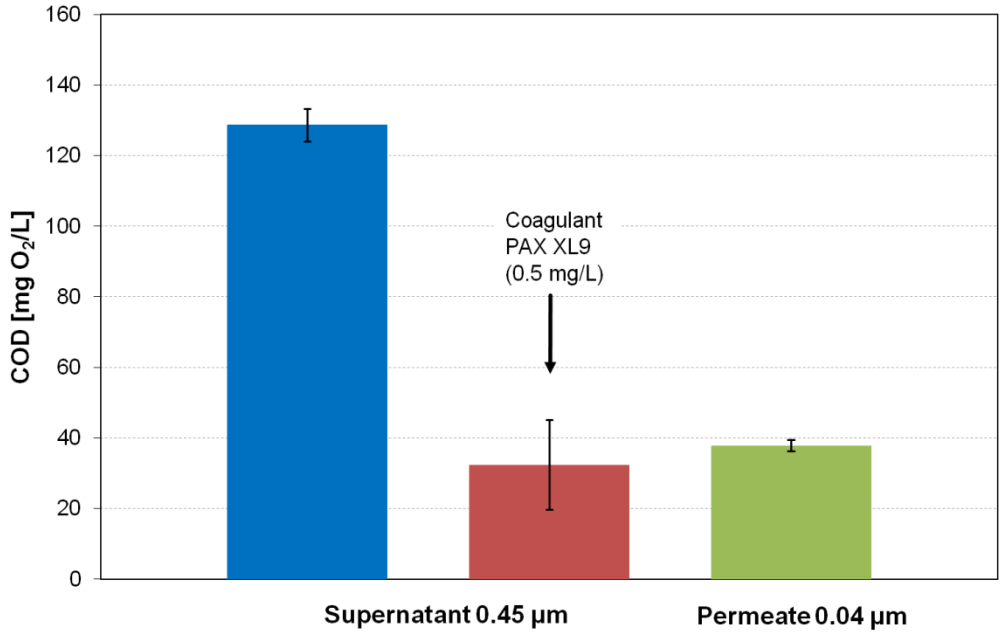


Figure 6-15: Comparison of COD concentration for supernatant samples (with and without the addition of coagulant) and permeate samples (Jar test).

Fractionation tests were performed for two periods; of stable operation (low fouling) and an incident with high concentration of organic matter and low temperatures at the same time (unsteady operation). These tests were to show the difference between the fractional compositions of organic compounds being degraded under different operational conditions. The experiments were carried out in batches.

As the membrane performance during unsteady conditions with high concentrations of organic matter sharply declined, the question arose whether a certain fraction of organic matter could cause severe fouling of the membrane. During this phase, the amount of organic fractionated matter in MBR was measured as COD and DOC concentration in the supernatant. *Figure 6-16* shows the COD and DOC percentage profiles of organic substances fractionated in accordance with size.

Whereas the fraction 0.04-0.1 μm constituted the largest percentage of COD (71 %) and DOC (81 %) of samples during high fouling in the MBR, this fraction made up only 21 % (COD) and 20 % (DOC) of samples during low fouling. However, during low fouling the fraction < 0.04 μm covered 59 % of the COD and 66 % of the DOC. The results show that biological degradation of organic matter was much higher during periods of low fouling. Only 41 % of organic compounds were retained by the membrane in the reactor compared to 84 % during periods of high fouling. Moreover, this implies that most of the biopolymers (proteins, polysaccharides) were retained in the reactor by membrane separation.

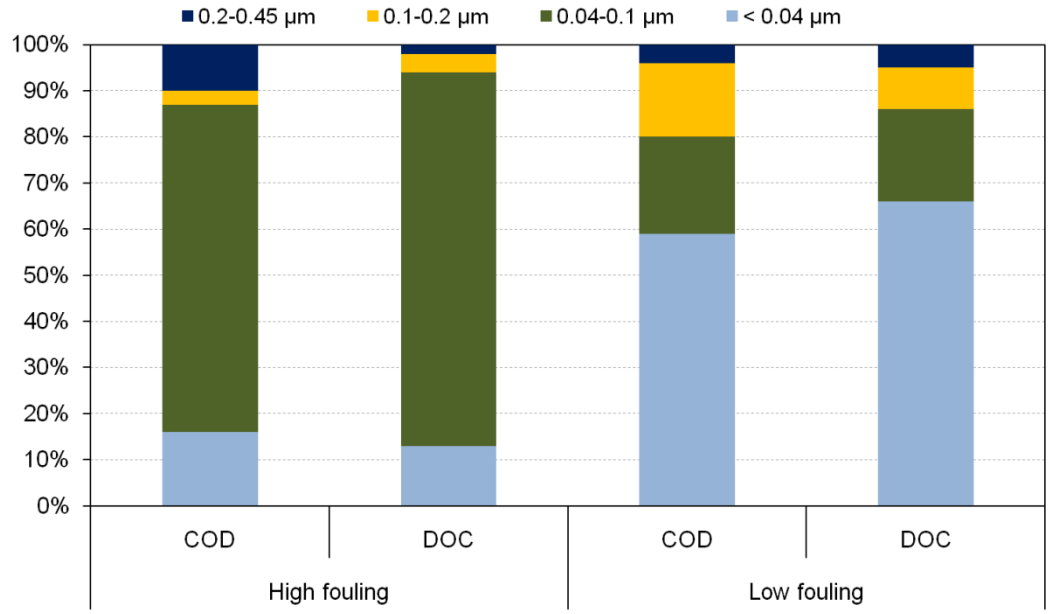


Figure 6-16: COD and DOC percentage profiles of organic substances with different sizes in supernatant and permeate during periods of high and low fouling potential of MBR.

Many authors identified SMP resp. EPS, also referred to proteins and polysaccharides, as the most significant factors responsible for membrane fouling (*Bouhabila et al., 2001; Cicek et al., 2003b; Rosenberger et al., 2006*). These substances can be formed by substrate metabolisms and presumably by biomass decay. Their concentration depends, inter alia, on stress conditions, to which microorganisms are exposed (*Barker et al., 1999*). Furthermore, triggers are, for example, extreme variations in temperature, SRT, influent composition, HRT, and MLSS concentration, etc. (*Schiener et al., 1998; Barker et al., 1999, 2000; Lee et al., 2001; Lee et al., 2002; Rosenberger et al., 2006; Drews et al., 2007*).

The above mentioned decline in permeability between the 510th and the 640th day could be caused by the retention of biopolymers (proteins, polysaccharides) by the membrane (see *Figure 6-17*). *Drews et al. (2007)* correlate rising membrane fouling at low temperatures, partly resulting from the retention of proteins and polysaccharides.

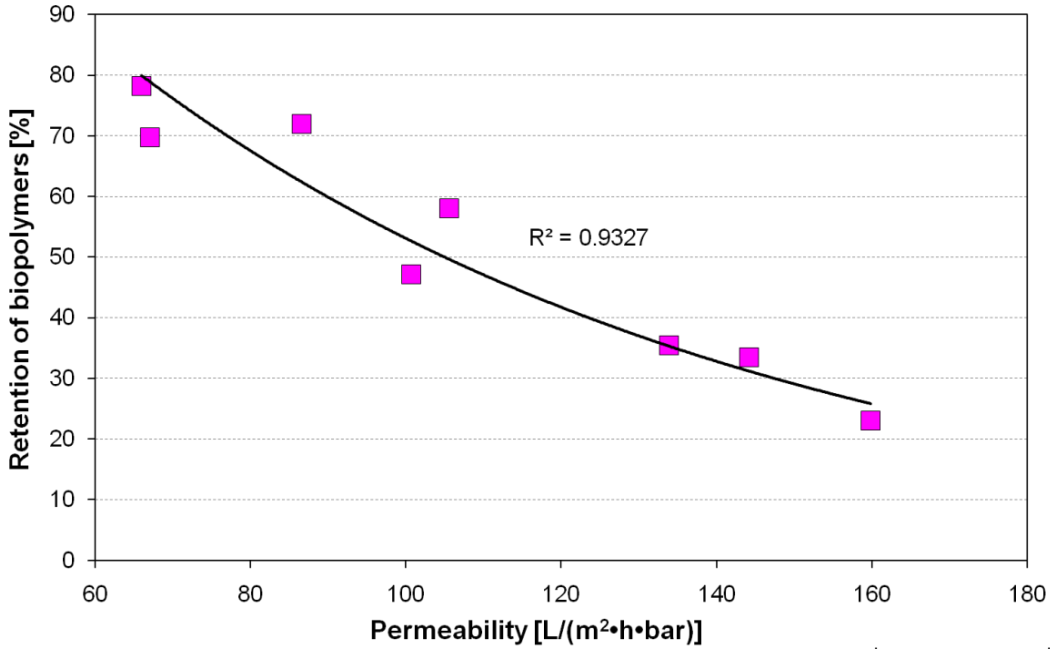


Figure 6-17: Retention of biopolymers vs. permeability between the 470th and the 648th day. The permeability was normalized to 20 °C.

Furthermore, a correlation was observed between the retention of biopolymers (proteins and polysaccharides) by the membrane and the CST of activated sludge (see *Figure 6-18*). Capillary suction time is used for the evaluation of the filterability, although causally it determines the dewatering characteristics of activated sludge. It was shown that the colloidal matter in the liquid phase of activated sludge cause poor filterability due to the organic compounds retained in the filter pores.

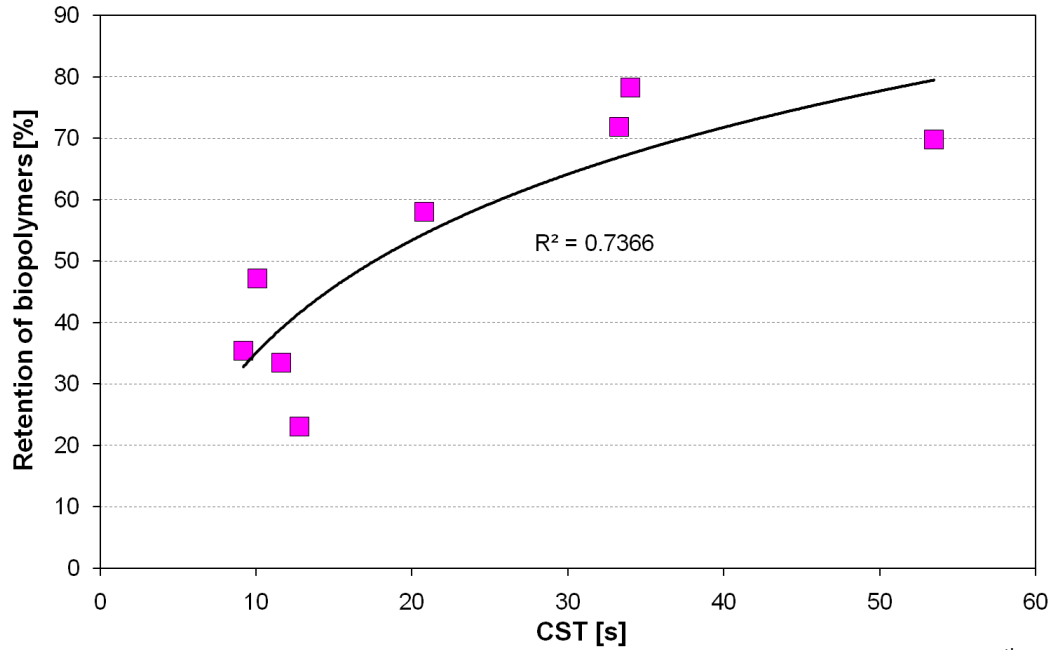


Figure 6-18: Retention of biopolymers vs. capillary suction time (CST) between the 470th and the 648th day.

Another important operating parameter that affects membrane fouling is SRT. However, SRT cannot be considered as direct fouling cause, but rather as parameter influencing various sludge properties,

such as floc size, settling characteristics, sEPS/SMP content etc., characteristics that are directly related to fouling rates (*Al-Halbouni, 2008*).

Moreover, SRT is an important parameter in order to ensure the advanced biological treatment of wastewater compounds and describes the period of time during which activated sludge remains in the system. SRT was calculated according to *equation 2.10*. Most membrane bioreactors (particularly in Germany and Switzerland) are currently operated at a sludge age of > 25 days (sludge stabilization) (*Wedi et al., 2008*).

Figure 6-19 shows the trend of permeability at different SRTs (between 10 and 35 d) as well as the colloidal matter (COD, proteins, polysaccharides) in the liquid phase of activated sludge. The investigation on the impact of SRT on the fouling behavior started one month after the phase of biomass growth. Starting with a MLSS concentration of 14 g/L, excess sludge was wasted daily and high SRTs of between 25 and 30 days were set. The experiments had to be stopped after two months due to operational disturbances (foaming, bulking) that lead to an enormous loss of biomass in the system. As SRT decreased, parallel high concentrations of colloidal matter were observed, also occurring in the following investigation phase at lower SRTs of between 20 and 25 days. However, no negative effect on the permeability was observed in the period between the 115th and the 250th day. The permeability decreased only slightly.

The experiments carried out at high SRT between the 280th and the 328th day had to be interrupted, again due to foaming and due to the replacement of the membrane module on the 345th day of operation. After an initial drop at SRTs between 30 and 35 days, the permeability of the replaced module stayed relatively stable. Starting at the 450th day, there was another shutdown due to foaming and bulking that resulted in the loss of biomass in the system. The decrease in MLSS automatically caused the decline of SRT.

Subsequently, the investigation at low SRTs of < 20 days was made possible by changing the tank volume. In comparison to the operation at high SRT, the significant decline in permeability was here observed at low SRTs of < 20 days. However, in the frame of this thesis it was not possible to find out, whether the sharp decline in permeability resulted from the decreasing SRT or possibly due to the occurrence of high concentrations of colloidal matter or whether they were interrelated. Differences in colloidal COD concentration of approximately 50 % and biopolymers (proteins, polysaccharides) of more than 100 % were also observed, between the first and the second occurrence of these high concentrations.

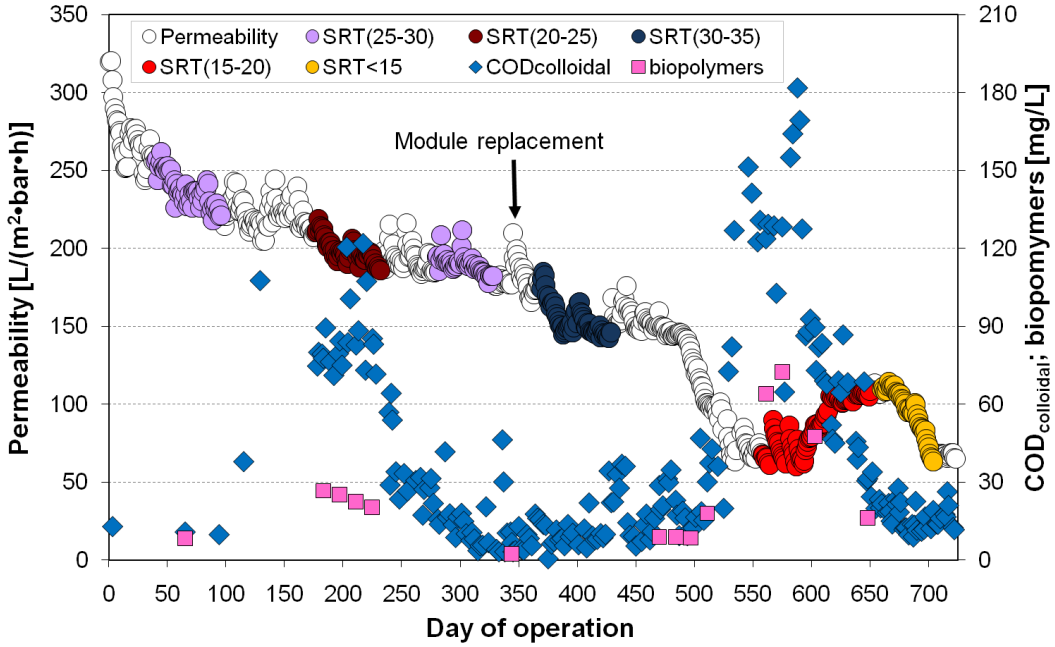


Figure 6-19: Trend of permeability at different sludge retention time (SRT) and colloidal matter concentrations in the supernatant of activated sludge within the investigation period. The permeability was normalized to 20 °C. All round symbols present the permeability but at different SRTs. White symbols show the permeability at no specific SRT.

There are many authors who describe a negative impact on membrane fouling by low SRT, by high concentrations of SMP or bound EPS (*Rosenberger, 2003; Grelier et al., 2006; Drews et al., 2008; Malamis et al., 2009*). Carbohydrates of SMP or soluble EPS, particularly the polysaccharide fraction in the supernatant, are often considered as major cause of membrane fouling in MBR (see *chapter 2.4.4.3*) (*Judd, 2004; Grelier et al., 2006; Rosenberger et al., 2006; Pan et al., 2010*). According to *Lee et al. (2001)* and *Cha et al. (2004),* the sludge loading rate increases with membrane fouling, resulting in the accumulation of soluble EPS in activated sludge. *Bouhabila et al. (1998)* report that there is no reduction in fouling until SRT reaches 30 days. A roughly similar behavior of fouling was seen at low SRTs. *Lee et al. (2002)* confirm this trend, however, the decrease in permeate flux was independent of SRT, but only above a certain value of SRT.

Figure 6-20 shows the effect of SRT on the concentration of biopolymers, in terms of MLSS concentration. Here, the biopolymers concentrations tend to decrease with increasing SRTs. This trend is confirmed by previous observations of *Rosenberger (2003)*, however for industrial wastewater. *Trussell et al. (2007)* report that the highest levels of colloidal material, total SMP, and soluble COD were obtained at the lowest mean cell retention time (MCRT) of 10 d, with the poorest filterability of mixed liquor at the same time.

Colloidal matter, i.e. biopolymers, tends to decrease with increasing SRT. Hence, it can be assumed that a large fraction of wastewater compounds or their decomposition products, such as proteins and polysaccharides, was measured in the supernatant of activated sludge. For a reliable description of fouling phenomena, probably a combination of several factors has to be considered, i.e. not only biopolymers amount but also physicochemical parameters in the system (temperature, SRT), and membrane characteristics.

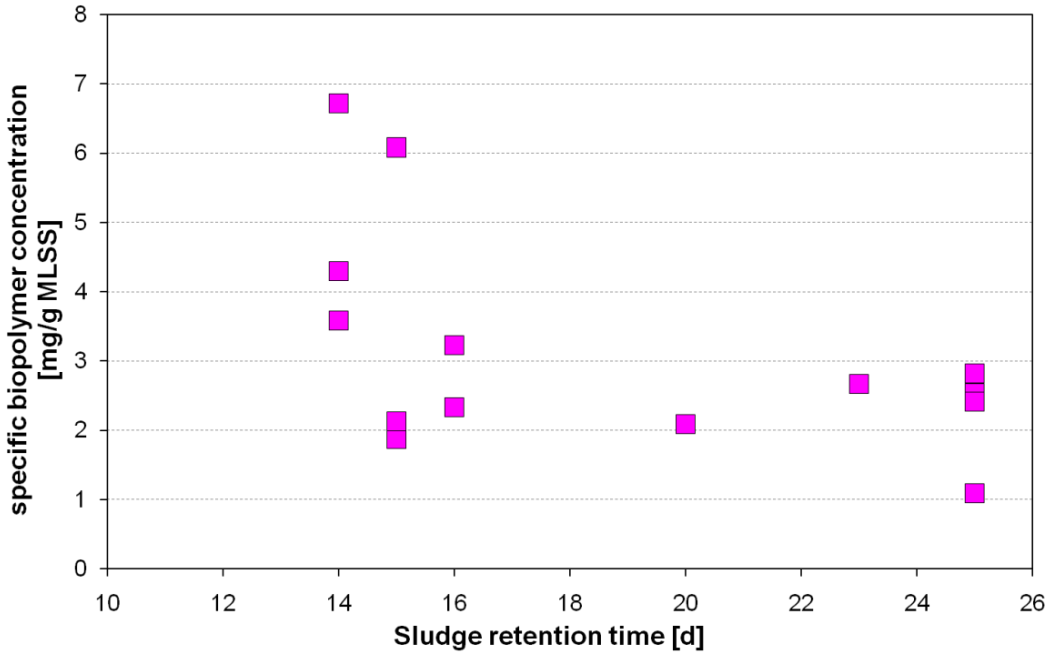


Figure 6-20: Effects of sludge retention time (SRT) on the specific concentration of biopolymers (proteins, polysaccharides) in the supernatant of activated sludge.

6.3.1.2. Truly soluble matter (< 0.04 µm)

In order to investigate the impact of truly soluble compounds, i.e. matter passing the membrane with nominal pore size of approximately 0.04 μm, on fouling, line#3 (downstream stage) was operated in series to the first membrane (line#1/line#2) at the MBR pilot plant (B) in Wiesbaden-Biebrich (see *Figure 6-21*). First, the investigation was performed at constant water flux between the 148th and the 218th day of operation, and then at increasing water flux between 219th and the 294th day.

Thus, the membrane of line#3 had contact with the same water containing the same dissolved matter $< 0.04\ \mu$m, but without colloids and particles $> 0.04\ \mu$m, as those were rejected by the first membrane (line#1/line#2).

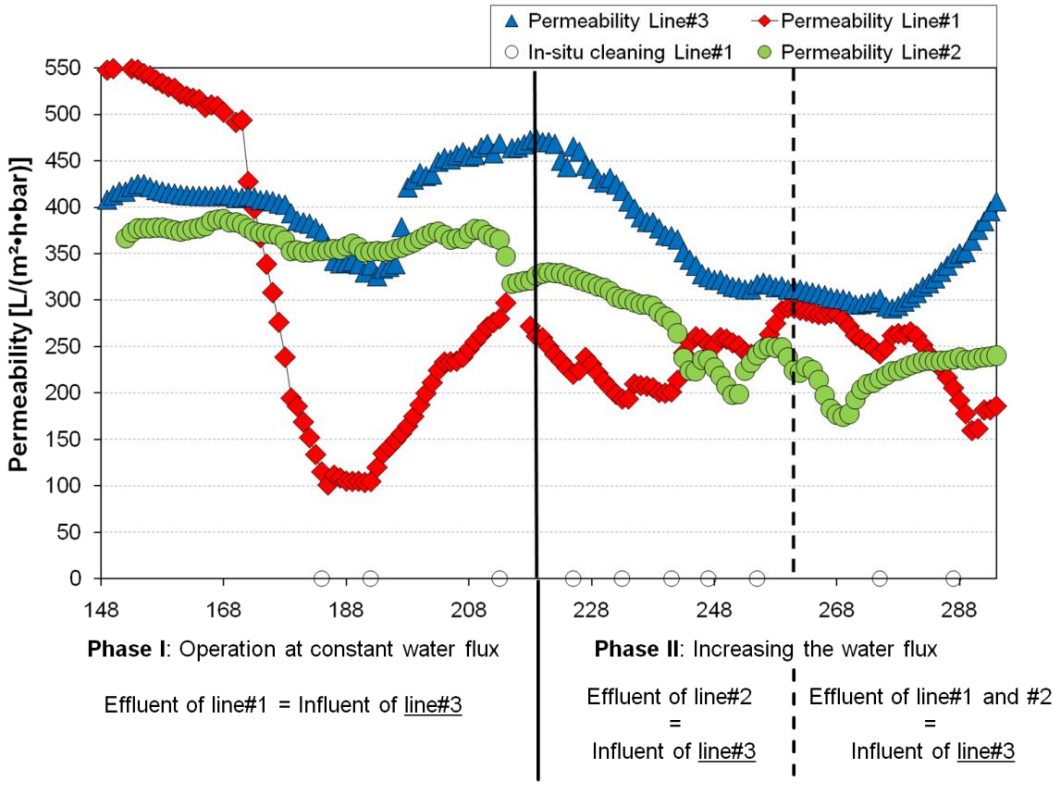


Figure 6-21: Overview of the trend of membranes permeability during the investigation on the impact of truly soluble compounds on fouling. The permeability was normalized to 20 °C.

Operation at constant water flux

In *Figure 6-22*, the trend of permeability of line#1 and line#3 (the effluent of line#1 = the influent of line#3) during 10 weeks of operation is depicted.

In order to enable a direct comparison of the membranes operated in parallel, the run of the permeability was related to the initial value of 100 %.

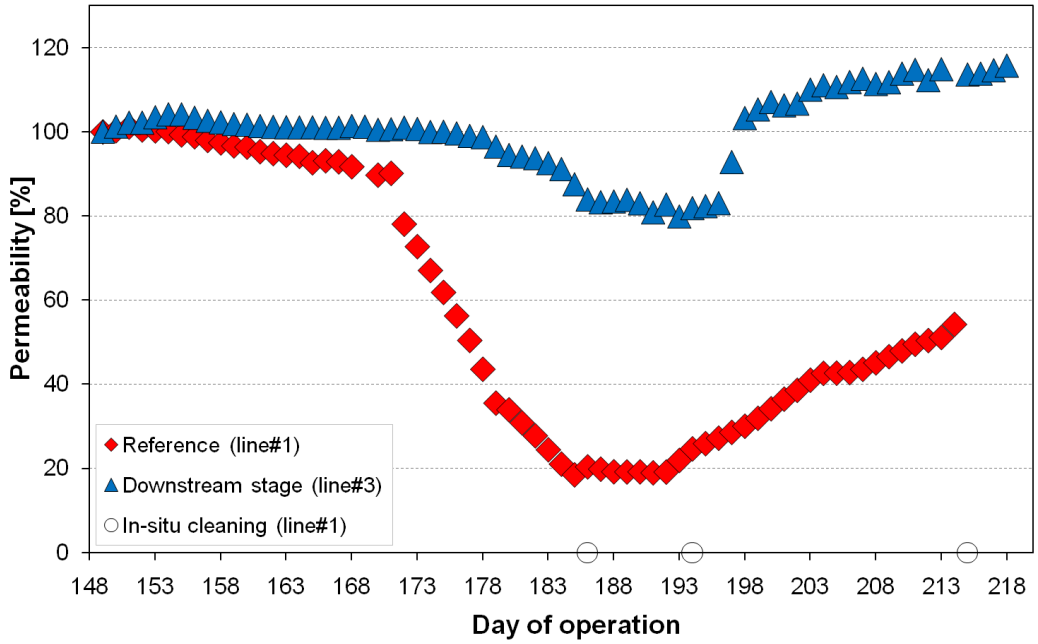


Figure 6-22: Comparison of permeability for pilot plant (B): line#1- reference without granulate, line#3 - sequential operation to line#1 (downstream stage) without granulate. The permeability was normalized to 20 °C.

Whereas the permeability of reference line#1 shows a significant decline from the 172nd day of operation on, there is only a slight permeability decrease in line#3. Both lines where operated at the same flux of 15 L/(m^2·h). It is important to note that the runs of the two curves are - each in its own level - synchronical. The truly dissolved constituents (< 0.04 μm) seem to affect membrane fouling only to a minor degree, whereas the decline in permeability of reference line#1 was caused predominantly by colloids and/or particles > 0.04 μm.

It should be mentioned again that the membrane of line#3 did not undergo any chemical cleaning, whereas the membrane of line#1 was cleaned with sodium hypochlorite on the 185th, the 193rd, and the 214th day (see *Figure 6-40*). It should also be noted that because the lines were operated in sequence, all changes in upstream lines could had a direct impact on the permeability performance of line#3, for example changes in the influent composition, flux or MLSS content, and of course the chemical cleaning procedure of reference line#1.

Increasing the water flux

In order to investigate the effect of truly soluble compounds at an enhanced water flux on the fouling potential of the membrane module operated in sequence, line#3 was first charged with the effluent of line#2 (from the 219th to the 260th day) (see *Figure 6-23a*) and then with the effluent of line#2 and line#1 (from the 261st to the 294th day) (see *Figure 6-23b*). It was not possible to charge line#3 only with the effluent of line#2, as its throughput was insufficient to operate line#3 at high flux rates.

Figure 6-23 shows the trend of permeability and flux rates of line#3, operated in sequence, and line#1/line#2, charging the downstream line#3, over the test period of 75 days.

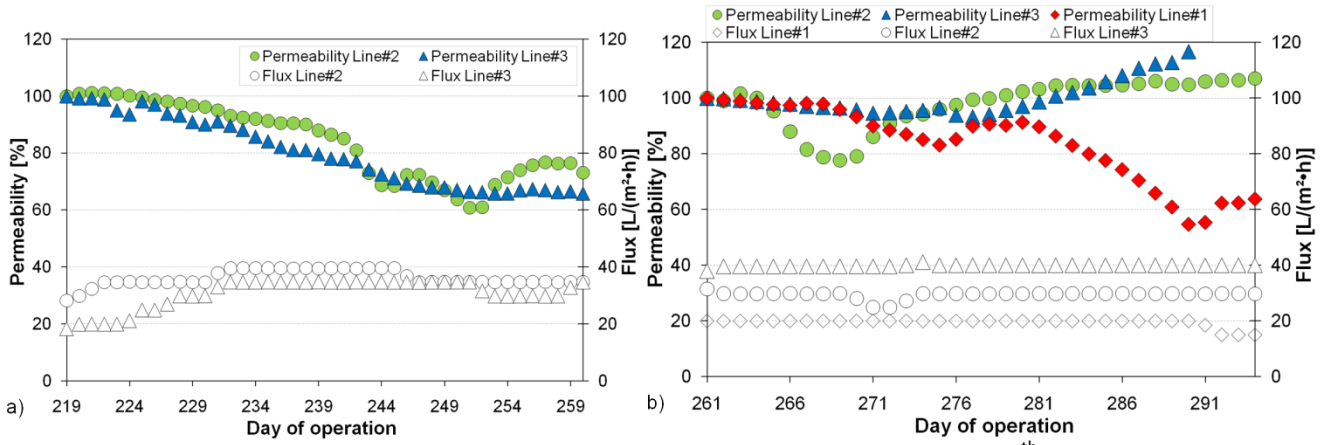


Figure 6-23: Comparison of line#2 - granulate and line#3 - next to line#2 until the 260th day and next to line#1 with line#2 from the 261st day in terms of permeability and flux during the test period. The permeability was normalized to 20 °C.

The flux of line#3 was adjusted from 20 to 35 L/(m^2·h) between the 219th and the 260th day and then increased up to 40 L/(m^2·h) between the 261st and 294th day of operation. A decline in membrane permeability of the line operated in sequence (line#3) was observed between the 219th and the 248th day of operation after the flux had been adjusted to 35 L/(m^2·h). However, the permeability recovered again as the flux increased up to 40 L/(m^2·h).

Thus, it is not clear whether the permeability decrease in the downstream line#3 between the day 219th and 248th day of operation was caused by the increase in flux rate or the effluent composition of line#2.

The impact of the individual components of mixed liquor, ranging from flocculent solids to dissolved molecules (e.g. polysaccharides, proteins) on membrane fouling, is discussed controversially in the literature. *Bae and Tak* (2005) state that the soluble products can be readily deposited onto the membrane surfaces by permeation drag, however not readily detached by shear force due to its low back transport velocity. *Defrance et al. (2000)* report the biomass relative contribution on fouling to be 65, 30, and 5 % for the suspended solid fraction, colloids, and dissolved matter, respectively. Others identify dissolved organics, such as polysaccharides and proteins, as well as organic colloids as the most significant factors responsible for membrane fouling (*Bouhabila et al., 2001; Cicek et al., 2003b; Rosenberger et al., 2006*).

Size exclusion chromatography/LC-OCD

During the whole experimental period, samples of filtered activated sludge supernatant (0.45 μm, Pall) of line#1 and line#2 as well as the effluent of line#1, line#2, and line#3 at the MBR pilot plant (B) were analyzed via gel permeation chromatography (LC-OCD). The respective chromatograms were evaluated in order to detect the soluble compounds of synthetic feed and/or activated sludge (mainly biopolymers) that could affect the permeability performance of the operated lines. The LC-OCD method enables the separation of organic dissolved compounds according to their molecular weight. The characteristic peaks of humic substances and organic acids appear in the 59th and the 63rd min, respectively. The biopolymers are detected roughly in the 38th min.

In *Figure 6-24*, typical LC-OCD chromatograms of supernatant and effluent samples, taken on the 238th day of operation, are compared. All other LC-OCD chromatograms are in *Appendix B.3*.

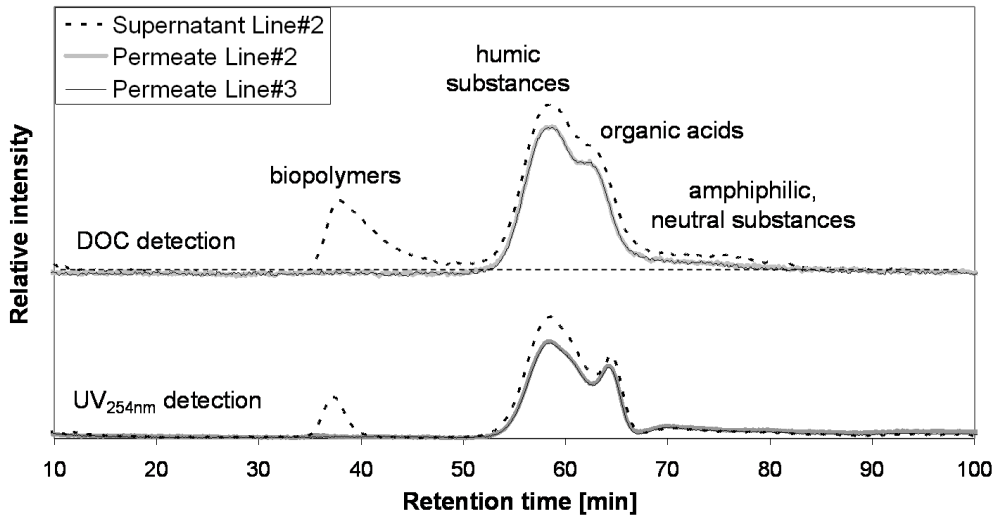


Figure 6-24: LC-OCD chromatogram of collected samples (supernatant and permeate of line#2, and permeate of line#3), taken on the 238th day of operation.

While the humic substances peak is almost parallel in all three samples, it is obvious that the biopolymer peak only appears in the supernatant sample, but not in the permeates (both DOC and UV detection). *Table 6-4* quantifies these observations.

Table 6-4: DOC_{total} and DOC of biopolymers of 0.45 µm filtered samples (line#2) and permeate (line#2, #3) taken on the 238th day of operation.

Sample	DOC_{total} [mg/L]	DOC of biopolymers [mg/L]	DOC of biopolymers [%]
Supernatant#2	5.0	1.0	20
Permeate#2	3.05	0.05	1.6
Permeate#3	2.79	0.04	1.4

The activated sludge supernatant of line#2 is composed of up to 20 % (DOC) from biopolymers and up to 80 % (DOC) from humic substances and low molecular fractions (organic acids, and neutral substances). As the UV detection also showed a peak at the respective retention time, it is possible that the detected biopolymers (DOC) consist of proteins, at least to some extent. Moreover, it is known that inorganic compounds, such as polyelectrolytes, polyhydroxy compounds, oxides/hydroxides of iron (III) and aluminum, can also be adsorbed by UV light at a wavelength of 254 nm (*Jiang, 2007*).

Thus, the main difference among the investigated samples were the biopolymers, which were detected only in the supernatant of the upstream line. Dissolved compounds (biopolymers) > 0.04 μm, which were rejected by the upstream membranes, could cause a decline in the permeability of these lines. This result recurred in all other analyzed samples.

6.3.1.3. MLSS

Viscosity

The activated sludge from the membrane bioreactor at the MBR pilot plant (A) in Darmstadt-Eberstadt showed a structural viscous behavior, i.e. the sludge viscosity decreased with increasing shear rate. This is due to the fact that the network structure of activated sludge flocs undergoes large scale breakage with increasing shear rate, resulting in a decrease in viscosity.

In addition to viscosity, the shear rate should be given special attention, due to the viscous behavior. *Günder (1999)* and *Krause (2005)* estimated the decisive shear rate to be 40 s^{-1} on the basis of the rising speed of air bubbles. In the following, viscosity at a shear rate of 40 s^{-1} is termed "apparent viscosity". However, it should be noted that the measurement uncertainty increases significantly at low shear rates, hence, the occurrence of viscous behavior can also be attributed to an error in measurement.

Figure 6-25 shows that the apparent viscosity can be correlated with the concentration of mixed liquor suspended solids. That means that with increasing MLSS concentration the viscosity also tends to increase. The viscosity amounts to 18 mPa·s at a "common" MLSS concentration of 12 g/L in MBRs and a shear rate of 40 s^{-1}.

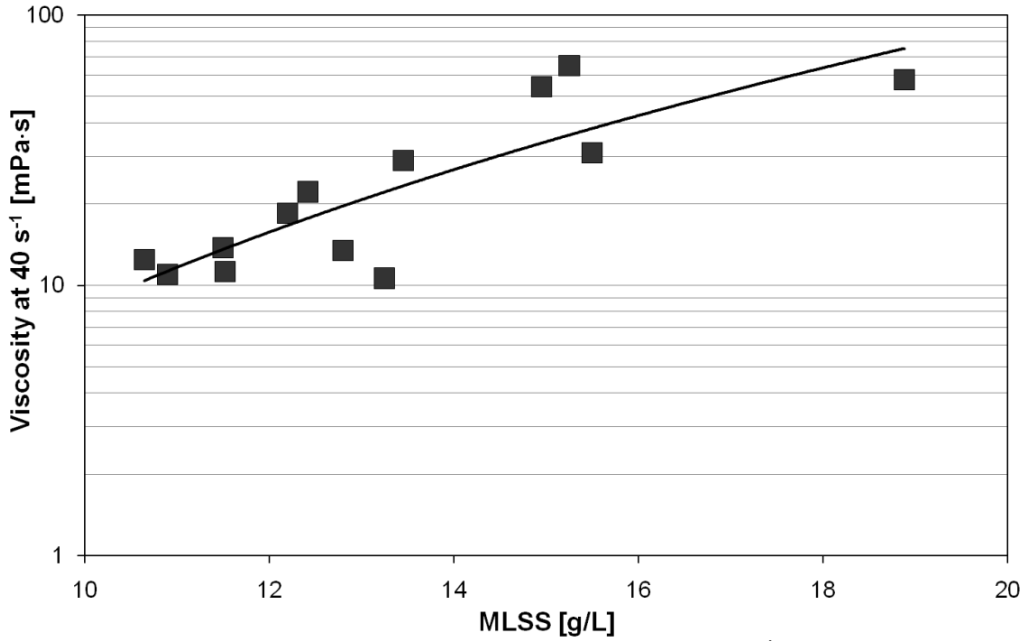


Figure 6-25: Viscosity vs. MLSS concentration at a shear rate of 40 s^{-1}.

Wastewater composition and the microbiological structure of activated sludge are also described as important factors for the apparent viscosity (*Rosenberger, 2003*). The formation of flocs or other cell aggregates is provided by EPS, which form a highly hydrated gel, keeping the microorganisms together. Sludge viscosity has been reported to increase with EPS concentration (*Nagaoka et al., 1996; Günder, 1999*).

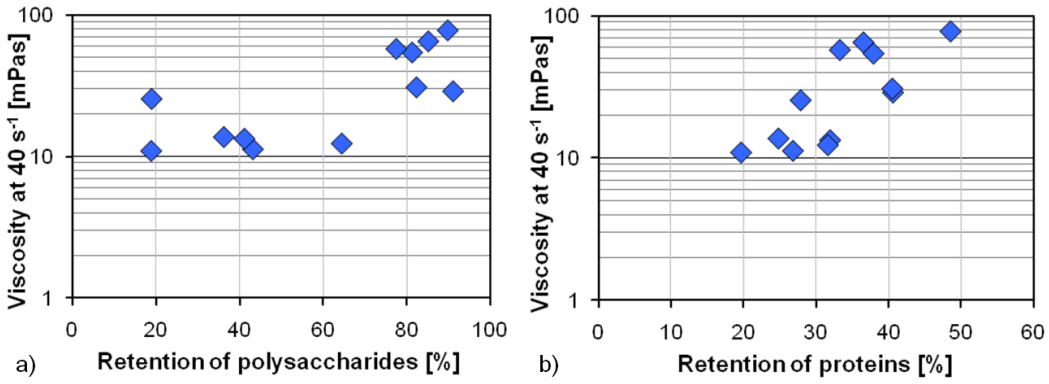


Figure 6-26: Viscosity as a function of polysaccharides (a) and protein retention (b).

Figure 6-26 illustrates the apparent viscosity as a function of polysaccharides and proteins retained in the mixed liquor filtrate of activated sludge. *Günder (1999)* explains the relationship between EPS (polysaccharides, polypeptides) and viscosity as an occurrence of interactions between biopolymer molecules. These interactions lead to a higher fluid viscosity.

Modeling approaches and parameter determination

All measured data were interpreted both with the approach of Oswald de Waele (structural viscous behavior without yield stress) and Herschel-Bulkley (flow curve with apparent yield stress) (see *Table 2-3*).

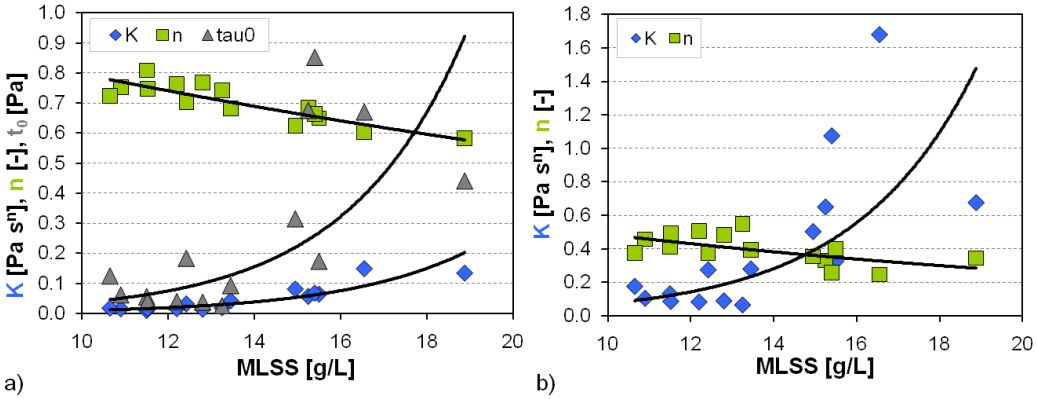


Figure 6-27: Model parameters according to the approach of Herschel-Bulkley a) and Oswald de Waele b) as a function of MLSS concentration.

The coefficients of both model approaches can be described as a function of MLSS concentration using a non-linear regression analysis (see *Figure 6-27*). For activated sludge investigated at the MBR plant (A) best results were obtained with an exponential regression for the consistency factor (K) and with an exponential regression for flow index (n), and yield stress (τ_0). The results of the regression analysis are shown in *Table 6-5*.

Table 6-5: Coefficients of both regression analyses.

Model	Model equation	Coefficient	Unit	R^2
Herschel-Bulkley	$\eta_s = \frac{\tau_0}{\gamma} + K \cdot \gamma^{n-1}$	$\tau_0 = 0.0009e^{0.3648 \cdot MLSS}$ $K = 0.0003e^{0.3411 \cdot MLSS}$ $n = 1.1431e^{-0.0362 \cdot MLSS}$	Pa $Pa \cdot s^n$ -	0.53 0.83 0.78
Oswald de Waele	$\eta_s = f(\gamma) = K \cdot \gamma^{n-1}$	$K = 0.0024e^{0.3398 \cdot MLSS}$ $n = 0.8884e^{-0.06 \cdot MLSS}$	$Pa \cdot s^n$ -	0.61 0.37

Table 6-5 shows that the correlation coefficients are lower for the approach of Oswald de Waele than for the approach of Herschel-Bulkley. In particular, the flow index (Oswald de Waele) shows a low value of 0.37.

The apparent viscosity at the shear rate of 40 s^{-1} was illustrated as a function of the MLSS concentration using the measured and calculated regressions (see *Figure 6-28*). It was found that both modeling approaches could map the data well. Though with the Herschel-Bulkley approach three different coef-

ficients were aligned, while the Oswald de Waele approach used only two coefficients, the latter showed a better plausibility with the measured values.

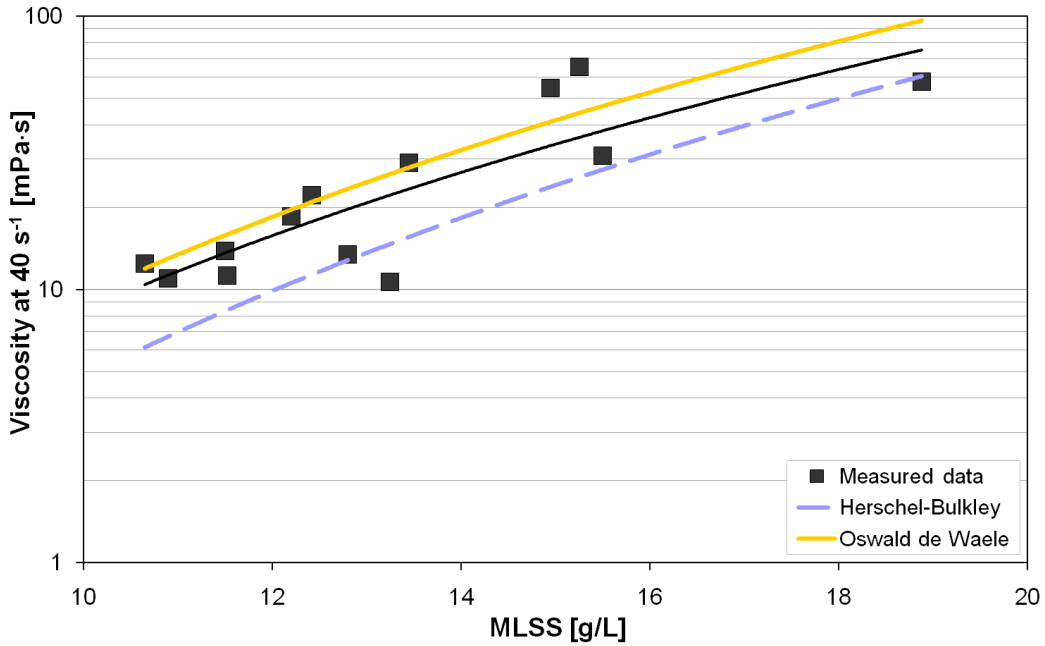


Figure 6-28: Comparison of modeling approaches with measured data for viscosity vs. MLSS.

The measuring methodology provides the advantage of good results reproducibility however, phase separation (decomposition) cannot be excluded during the measurement, as MBR activated sludge presents a three-phase system consisting of suspended solids, liquid (water), and gases (air).

6.4. Research on fouling reduction

6.4.1. Application of granulate material

6.4.1.1. Experiments with selected granulate – test phase I

In preliminary investigations on the selection of granular material at the MBR pilot plant (B) in Wiesbaden-Biebrich, line#1 (reference), line#2, and line#3 were operated in parallel at the same MLSS concentration of 4 g/L ± 1.9. However, line#2 and line#3 were additionally operated with granular material (see *Table 4-6*) at concentrations of 5 kg/m^3 between the 1st and the 34th day of operation and then 4 kg/m^3 from the 35th day.

Variations in crossflow velocity were performed for choosing the most appropriate airflow rate, under which granular material moved into the loop. Three airflow rates (3 m^3/h, 5 m^3/h, and 7 m^3/h) respectively specific aeration demand per membrane area SAD_m 0.3-0.7 m^3/(m^2·h) were tested. Although the tests were performed in accordance with the values given for current membrane systems 0.2-0.8 Nm^3/(m^2·h) (*Judd, 2006; Guglielmi et al., 2008; Verrecht et al., 2008; Grélot et al., 2009; Lorain et al., 2010*), the most appropriate SAD_m for the granular material of being moved into the loop was 0.7 m^3/(m^2·h). It was observed that the short-term operation with the granular material at SAD_m > 0.7 m^3/(m^2·h) led to irregular distribution of the granular material, mostly in the upper part of the

filtration tank as a result of the attachment of air bubbles on the surface of the granular material. The results also show that the granulates were not hold in a state of suspension at $SAD_m < 0.7\ m^3/(m^2 \cdot h)$. Thus, it was found that the optimal SAD_m for this experiment was $0.7\ m^3/(m^2 \cdot h)$.

During six weeks of operation, the cleaning performance of granulate was investigated at flux rates between 10-15 $L/(m^2 \cdot h)$ and compared with the reference line. Since declines in permeability are important to evaluate fouling behavior, data on permeability changes were gathered for each membrane module. In this respect, first results of the test phase are shown in *Figure 6-29*.

The initial permeability values of membrane modules operated with granulate were between 300 $L/(m^2 \cdot bar \cdot h)$ and 500 $L/(m^2 \cdot bar \cdot h)$. As long as granulate circulated in filtration tanks, the permeability stayed at high levels. As a result of granulate settling, the permeability of the membrane operated with PMMA granulate declined significantly from the 33rd day. Although the permeability of the reference module (without granulate) was initially about 500 $L/(m^2 \cdot h \cdot bar)$, the permeability decreased to about 55 $L/(m^2 \cdot h \cdot bar)$ within one month of operation. Consequently, it was necessary to clean the reference module by using NaOCl and citric acid as early as the 30th day of operation. Despite chemical cleaning, the permeability stayed above 100 $L/(m^2 \cdot h \cdot bar)$ for only two days.

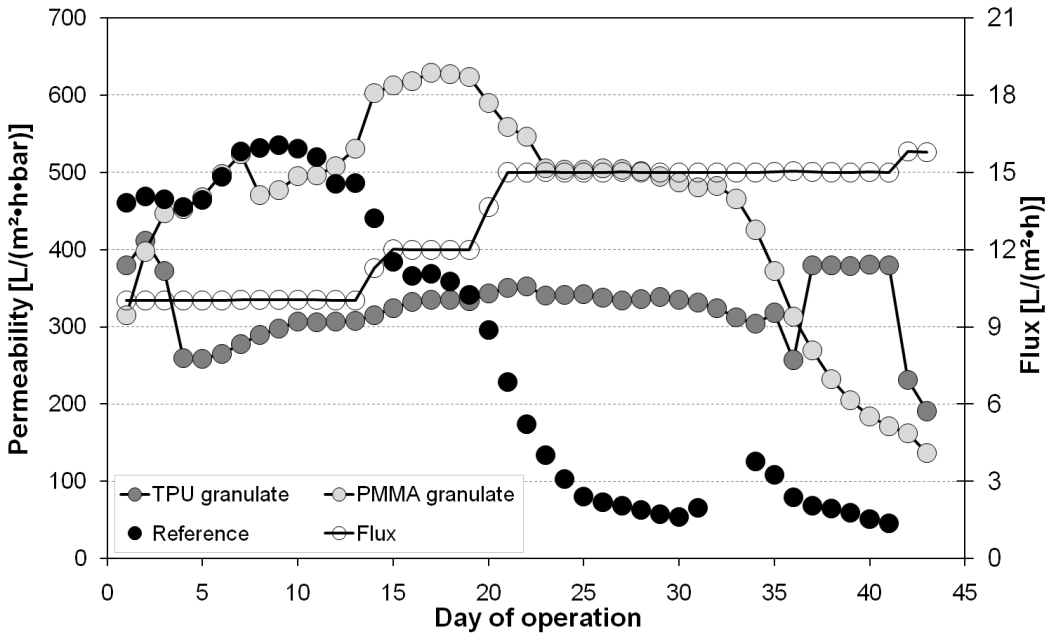


Figure 6-29: Trend of permeability and flux during test phase I with synthetic wastewater. The permeability was normalized to 20 °C.

The results show that granulate had a positive effect on the permeability. Moreover, during the whole test period, chemical cleaning was not necessary for both membrane modules operated with granulate. After these successful preliminary investigations with granulate, it was decided to perform long-term tests, however, a lighter granular material with a density of about 1 kg/L was chosen in order to avoid the settling effect in the filtration tank.

Table 6-6 shows the comparison of both lines operated with granulate (TPU and PMMA) and the reference line (without granulate) over the operating period of 43 days. During this short-term operation, the membrane modules operated with granulate (TPU and PMMA) reached throughputs of 15.7 m^3 and 20.21 m^3, compared to 87.3 m^3 in the reference line. Hence, the enhanced membrane throughput

of the TPU and PMMA lines was about 15.7 m^3 and 20.21 m^3, viz. approximately 15.2 % and 18.8 %, higher than the throughput of the reference line.

Table 6-6: Comparison of the lines operated with granulate and the reference line (without granulate) during the investigation.

	Reference line	Granulate line (TPU)	Granulate line (PMMA)
Operating period	41 d	43 d	43 d
Total membrane throughput	87.3 m^3	103 m^3	107.5 m^3
Difference		**+15.7 m^3 (+15.2 %)**	**+20.21 m^3 (+18.8 %)**
Average flux rate (gross)	12.8 L/(m^2·h)	13.1 L/(m^2·h)	13.3 L/(m^2·h)
Average flux rate (net)	9.9 L/(m^2·h)	10.5 L/(m^2·h)	10.6 L/(m^2·h)
Number of chemical cleaning measures	1 MC[1] 1 IC[2]	0	0

[1]- Maintenance cleaning

[2]- Intensive cleaning

6.4.1.2. Permanent use of granulate material during MBR operation with synthetic and real wastewater – test phase II

During subsequent tests, two membrane modules were operated in parallel, whereby in addition to line#2 – operated with an oval polypropylene granulate (PPTV20) at a concentration of 4 kg/m^3 (see *Table 4-6*) – reference line#1 was tested. Analog to test phase I, the cleaning performance of granulate was investigated over two years of operation and compared with the reference line.

The run of the permeability and flux curves for line#2 of the plant, operated with synthetic wastewater and holding granulate - are shown in *Figure 6-30* for the whole test period. The initial permeability was about 360 L/(m^2·h·bar) and stayed more or less constant at a flux of 15-30 L/(m^2·h) within the first 200 days of operation. As a result of increasing the flux from 35 up to 40 L/(m^2·h) between the 210th and the 260th day, the permeability declined significantly from 360 to 200 L/(m^2·h·bar). During further operation, the initial permeability did not recover, even after decreasing the flux level again. It seems that MBR operation at high flux rates of 35-40 L/(m^2·h) leads to irreversible fouling inside the membrane pores that cannot be removed by granulate. According to *Chen et al. (2006)* and *Jönsson (1995)*, this might be caused by permeation drag force. High flux rates as well as high filtration pressures may cause stronger permeate drag forces on particulate and colloidal matter, acting perpendicular to the membrane surface and leading to increased membrane fouling. Zhu and *Elimelech (1995)* report that permeation drag forces play an important role in particle deposition on membrane surfaces and may finally control the rate of colloidal fouling. According to *Bacchin et al. (2002)*, a significant flux increase causes an enhanced accumulation of rejected macromolecular particles on the membrane surface, the so-called “concentration polarization” phenomena. During the next 100 days of operation, at a constant flux level of 30 L/(m^2·h), the permeability stayed relatively constant in the range between 200 and 250 L/(m^2·h·bar).

After about 370 days, it was observed that possibly due to the decrease of the F/M ratio (food to microorganisms) (see *Figure 6-9*) the sludge characteristics in the plant changed, in terms of decreasing filterability, an increase in the CST, and foaming. At the same time, a permeability decline to about 150 L/(m^2·h·bar) was observed, although the flux was reduced to 20 L/(m^2·h). Finally, after the sludge had been replaced against fresh sludge (ca. 0.74 m^3) from a MBR pilot plant of Microdyn-Nadir on the 449th day of operation, the plant was set to the previous operating conditions with a SRT > 25 days. Parallel, the flux was decreased again to 15 L/(m^2·h) and thus, the permeability stayed constant until to date (> 600 days). During the whole experimental period of currently 622 days of continuous operation, no chemical cleaning in the granulate holding line#2 has been carried out.

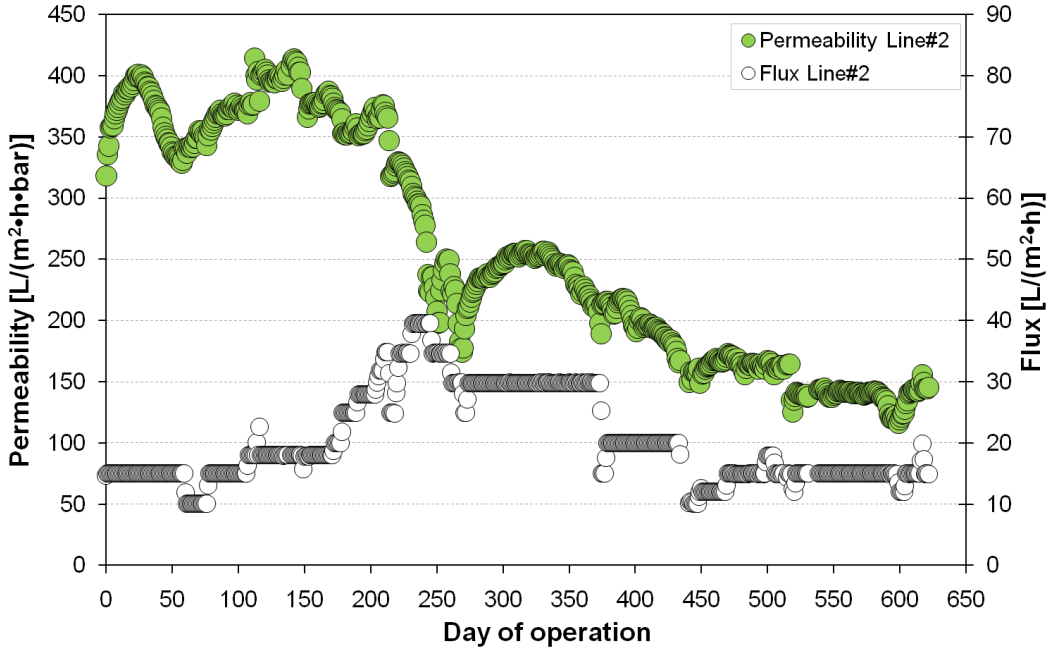


Figure 6-30: Trend of permeability and flux during tests with synthetic wastewater. The permeability was normalized to 20 °C.

In *Figure 6-31*, the results of the MBR plant operated with real wastewater are depicted. After an initial permeability loss of nearly 20 %, the permeability stayed constant over 100 days of operation at a flux between 10 and 14 L/(m^2·h), although the MLSS content increased from 4 to 21 g/L. No backwash with permeate, no relaxation breaks nor chemical cleaning were performed within that test period. It is concluded that permanent mechanical cleaning by granulate prevents membrane fouling and permeability loss, which would have been expected for the operation without granulate. Hence, it was shown that the findings from the MBR pilot plant (B) operation with synthetic wastewater could also be applied to real conditions (MBR plant C). Moreover, mechanical cleaning via adding granulate showed that the formation of unwanted fouling layers was reduced as a result of abrasion processes and by augmentation of back diffusion as granulate improves the mixing of the liquid at the membrane. Thus, a new method with a high potential for effective and economic fouling control of membranes was developed in long-term MBR operation experiments, in which no negative impact on the effluent quality was observed.

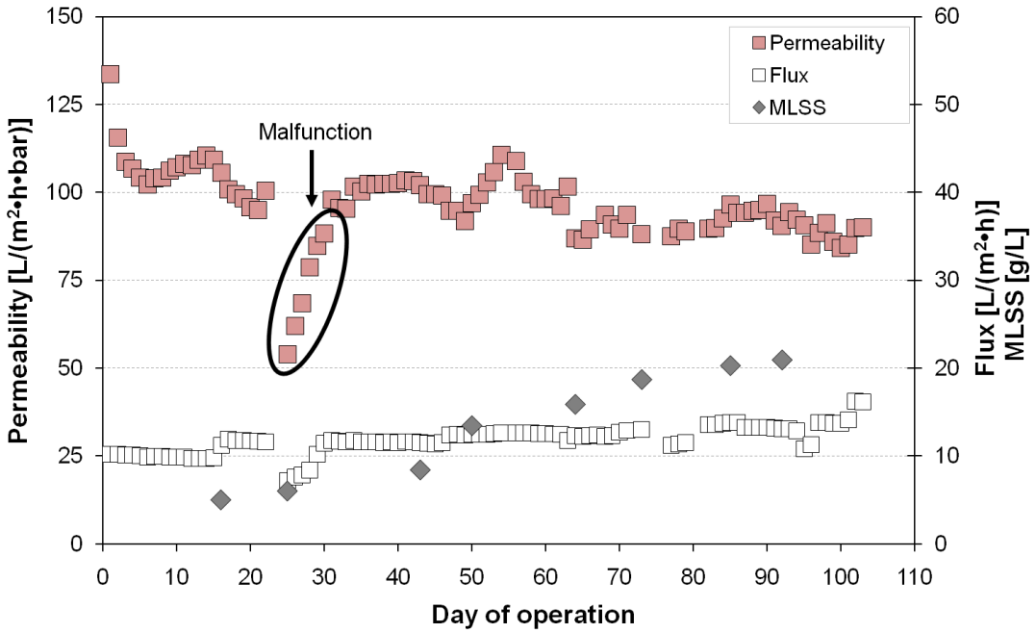


Figure 6-31: Trend of permeability, flux, and MLSS concentration during tests with real wastewater. The permeability was normalized to 20 °C.

6.4.1.3. Granulate material contra conventional MBR operation

Line#2 with granulate was operated in parallel to reference line#1 without granulate at the same flux of 14 L/(m^2·h) and identical MLSS of about 10 g/L for more than 100 days. Whereas the permeability of line#2 stayed more or less constant over that period, line#1 showed a significant decline in permeability of about 60 % within the first 68 days (*Figure 6-32*) as a result of membrane fouling. It should be mentioned that line#1 needed some in-situ membrane cleaning (NaOCl, 1,000 ppm) to maintain the permeability at around 100 L/(m^2·h·bar) from the 79th day on, whereas line#2 was not cleaned at all.

Thus, the observed differences are only attributed to the cleaning effect of granulate. The new mechanical cleaning procedure passed also in terms of environmental impact and sustainability. As no cleaning chemicals are used, no byproducts, e.g. AOX (organic halogen compounds) by using NaOCl, are produced. Furthermore, abandonment of chemicals positively affects the membrane's lifetime. The flux of line#2 with granulate was increased to 40 L/(m^2·h) little by little after 100 days of operation. As line#1 could not handle higher flux rates, a direct comparison of the lines was not possible afterwards.

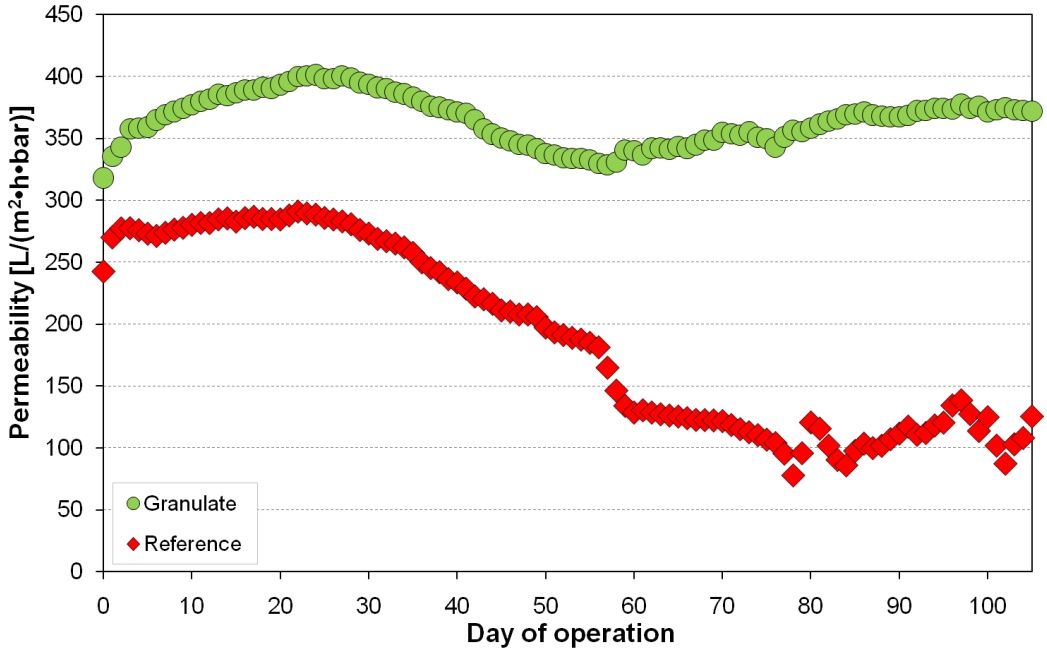


Figure 6-32: Trend of permeability for reference without granulate (line#1) and with granulate (line#2) under the same operating conditions. The permeability was normalized to 20 °C.

6.4.1.4. Permeability recovery of the conventionally operated membrane module

To investigate whether the permeability of "blocked" membranes can be restored by mechanical cleaning, granulate (same material as line#2) was added to reference line#1 for a short time on the 114th day of operation and then removed again. The results are presented in *Figure 6-33*. Within one week, the permeability increased from 100 to 500 L/(m^2·h·bar), probably due to abrasion of the filtration cake on the membranes.

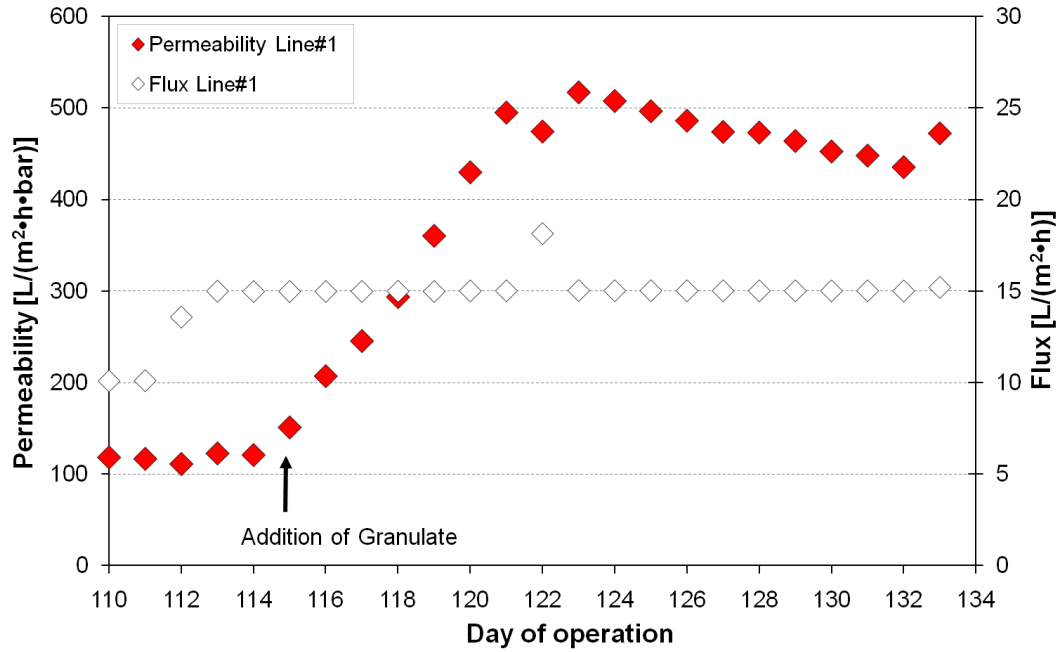


Figure 6-33: Effect of short-term addition of granulate to reference line#1. The permeability was normalized to 20 °C.

6.4.1.5. Granulate as flux enhancer

Table 6-7 shows the comparison of line#1 and line#2 during the investigation. During 622 days of continuous operation, line#2 (with granulate) was run at flux rates between 10 and 40 L/(m^2·h), whereas reference line#1 (without granulate) could only be operated in the range of 10-20 L/(m^2·h). The total membrane throughput of reference line#1 was about 1912 m^3, compared to 2433 m^3 in line#2. Hence, the enhanced membrane throughput of line#2 was about 521 m^3, viz. approximately 27 %, higher, although the line#2 was not cleaned chemically as the reference line#1 was. Achieving higher flux rates with granulate, directly translates to less membrane area and thus lower capital and maintenance cost, as less energy and chemicals are needed.

Table 6-7: Comparison of line#1 and line#2 during the investigation.

	Reference line	**Granulate line**
Operating period	622 d	622 d
Total membrane throughput	1912 m^3	2433 m^3
Difference		**+521 m^3 (+27 %)**
Average flux rate (gross)	16.2 L/(m^2·h)	20.6 L/(m^2·h)
Average flux rate (net)	13.3 L/(m^2·h)	16.7 L/(m^2·h)
Peak Flux (> 2 weeks)	20 L/(m^2·h)	40 L/(m^2·h)
Number of chemical cleaning measures	32 MC[1] 2 IC[2]	0

[1]- Maintenance cleaning

[2]- Intensive cleaning

6.4.2. Investigation of membrane material after granulate application

In the previous chapter, it was shown that granulate can enhance significantly the performance of ultrafiltration membranes as the flux rates are increased considerably. However, during mechanical cleaning by granulate, there is a potential risk that while removing the fouling layer on the membrane surface, the membrane material is damaged as a result of abrasive cleaning. For this reason, membrane samples were taken in order to assess the impact of granular material on membrane surfaces.

Wasp et al. (1997) describe two kinds of damage, i.e. cutting wear and deformation wear that can be caused by granulates colliding against the membrane surface. Cutting wear is mainly due to motion of particles along the membrane and would increase the permeability of a membrane, whereas deformation wear is due to motion perpendicular to the membrane surface and would rather reduce the permeability. The membrane can be deformed or impressed by a collision with granulates, when the stress in the membrane exceeds the elastic limit (*Noordman, 2000*).

6.4.2.1. SEM images

The morphology of membrane surfaces was analyzed by means of a SEM. The SEM images of the outer surface of membranes operated with TPU and PMMA granulate (test phase I) clearly show scratches and folds after 43 days of operation due to granulate collisions (see *Figure 6-34*). The membrane operated with TPU granulate seems to be more damaged as that with PMMA. As TPU granulates

are slightly larger and heavier (see *Table 4-6*) it can be concluded that the risk of membrane damage increases with increasing granulate size or density. However, the visual marks do not necessarily indicate membrane damage. All other SEM images are in *Appendix B*.

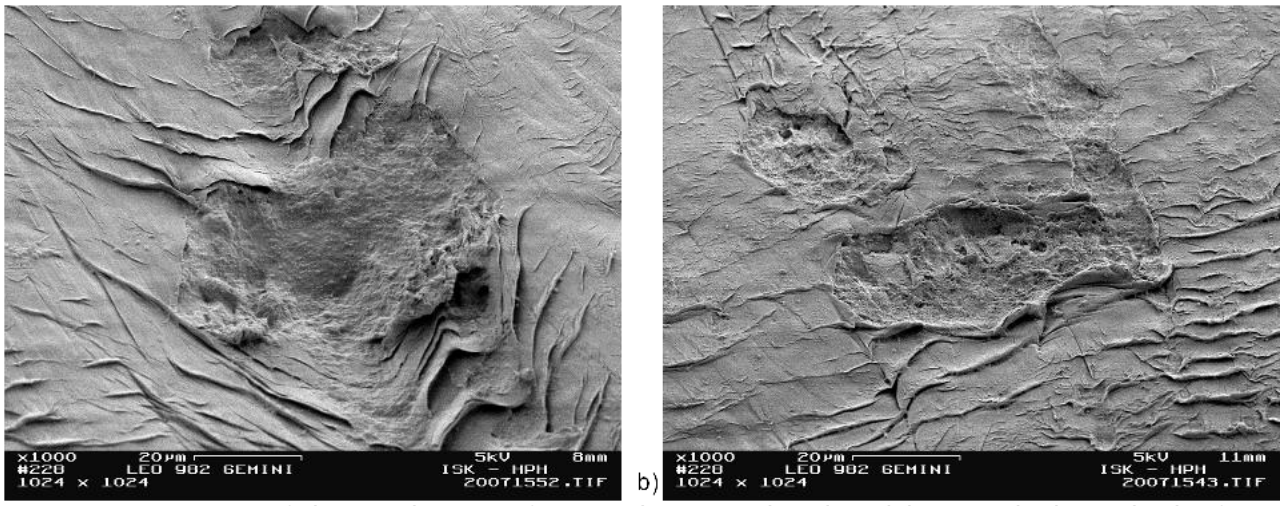


Figure 6-34: SEM images of the membrane surfaces at the MBR pilot plant (B) in Wiesbaden-Biebrich after 6 weeks of operation (test phase I); a) TPU granulate and b) PMMA granulate. The samples were magnified 1000 times.

In *Figure 6-35*, the respective outer surface of reference membrane (line#1) and membrane material after more than two years of operation with granulate (line#2) is depicted (test phase II).

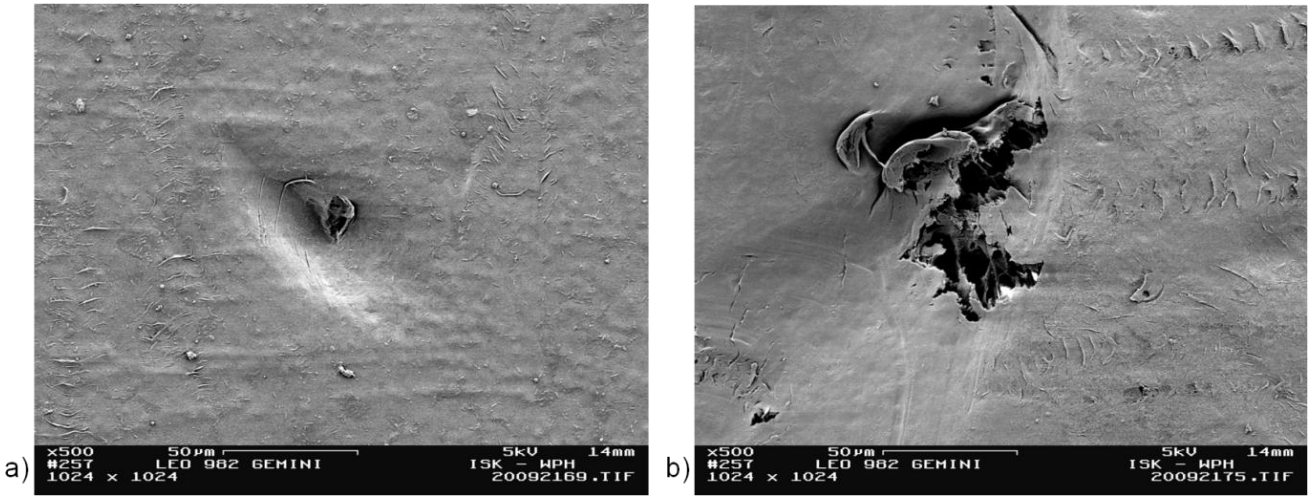


Figure 6-35: SEM images of the membrane surfaces at the MBR pilot plant (B) in Wiesbaden-Biebrich after 25 months of operation (test phase II); a) reference line#1 without granular material and b) after the use of granulate (line#2). The samples were magnified 500 times.

The SEM image of reference line#1 (see *Figure 6-35a*) clearly shows a fairly smooth surface without any folding, although with one noticeable point mark. Comparing the SEMs, it is obvious that the granular material left marks (folding and collision marks) on the membrane surface (see *Figure 6-35b*). However, these collision marks do not necessarily indicate membrane malfunction. The images only show the surface condition of the membrane skin and do not disclose the condition of the porous structure of the membrane. That is why integrity tests were performed in order to estimate the actual functioning of the membrane material. It should be noted that there is a risk that membranes are damaged even during installation and dismantling of the facilities and not only because of the impact of granulate.

6.4.2.2. Integrity tests

Rejection measurements

The main purpose of the integrity tests (flux and rejection) was to check whether the membrane properties had changed due to damages, thus leading to the reduced rejection of a test substance with given size distribution. The membrane rejection rates for a defined test substance were calculated according to *equation 2.7*. For the rejection measurement, a test solution was used in order to determine the apparent MWCO of the membrane. The minimum rejection rate of this test solution is > 90 % for new membranes.

The results of rejection measurements for membranes operated with TPU and PMMA granulate showed that these membranes were slightly damaged due to an abrasive effect (see *Table 6-8*). The rejection measurements for the membrane cleaned with TPU granulate showed significantly worse results (49.6 % ± 19.2) than for PMMA granulate (69.8 % ± 27.7).

In contrast to the membrane modules operated with granulate, the rejection measurements for the reference membrane showed significantly higher values of 95.5 % ± 0.8, thus consistently with a new membrane (> 90 %). The results indicate that in MBR applications PMMA granulate should be used rather than TPU granulate.

Table 6-8: Rejection measurements for membranes operated with granulate and for the reference membrane (without granulate) after six weeks of operation (test phase I).

	TPU granulate	PMMA granulate	Reference
Rejection measurements [%]	49.6	69.8	95.5
Standard deviation [%]	± 19.2	± 27.7	± 0.8
Number of samples	10	10	6

The membrane of the MBR pilot plant (B) in Wiesbaden-Biebrich, line#2, showed rejection rates of 89.9 % ± 3.4 after 25 months of operation (test phase II). Thus, no damaging effects by granulate could be observed, as the rates were more or less comparable to those of new membranes (95.1 % ± 1.9). Moreover, the rejection rate of the reference membrane (87.4 % ± 9.9) was even lower than that of the membrane operated with granulate.

In contrast, the rejection rates of the membranes used in the MBR plant (C) in Wiesbaden-Biebrich dropped significantly to 40 % ± 29. It is possible that the membrane damage was caused by the high momentum of the granulates. Their velocity was higher than for the MBR pilot plant (B) in Wiesbaden-Biebrich due to higher SAD_m of 0.8 $m^3/(m^2 \cdot h)$ and due to a low initial MLSS concentration of 4 g/L. All the same, the effluent quality (COD and turbidity) remained superior.

Water microbiology testing (total coliforms, E. coli)

In order to control whether the membrane operated with granulate still rejects viable bacteria, integrity tests of microbial removal for the two common water-related bacteria indicators, viz. Escherichia coli and total coliforms, were conducted. As the investigated membranes are in the range of ultrafiltration (0.04 μm), they are also able to retain bacteria.

Cutting wear of the membrane due to granulate could increase not only the rejection rates but also the number of bacteria in the sample. In order to exclude the positive effect of fouling residuals on the

retention rates, the used membranes were cleaned using citric acid (2 %) and NaOCl (100 ppm). In addition, the testing unit was also cleaned and disinfected. Blank tests with distilled water were performed shortly before measuring the actual samples. Despite the sterile experimental conditions and chemical cleaning, some coliforms were detected, however only in the blank test for one sample of new membrane. This might have been caused by insufficient disinfection of the backside of this membrane sample. In other cases, there were no bacteria in the permeate of the blank test.

Each membrane sample was charged with 300 mL of the input (supernatant), which contained 29900 mpn/100 mL of Escherichia coli and 105400 mpn/100 mL of total coliforms. As 200 mL of clear permeate was filtrated under certain conditions (200 mbar, 300 rpm, 20 °C) in the testing unit, an accumulation (concentrating) of bacteria in the input up to 3 times occurred. The accumulation factor (N) was calculated according to *equation 5.1*.

Figure 6-36 shows the mean values of Escherichia coli and total coliform bacteria in the influent and log removal of the bacteria for a new membrane, reference, and membrane operated with granulate. The results represent mean values of two determinations per test sample. The new membrane removed 4.5 logs (100 %) and four of five logs of Escherichia coli and total coliforms, respectively. The membranes operated with granulate and the reference line, which had rejection rates between 87.4 % ± 9.9 % and 89.9 % ± 3.4 %, with the test solution, showed bacteria removal of E. coli and total coliforms still to be 3 logs. These results indicate that the granulate did not have any negative impact on the membranes and still reject almost all bacteria in the system. The presentation of the complete removal of bacteria as „log removal“ is not representative for ultrafiltration membranes. In this case, it is recommended to express the removal of bacteria in percentages.

There were some bacteria detected in the effluent of all investigated membranes. However, this is probably due to microbial colonization of a section of the system piping rather than to bacterial penetration of the new membranes. Moreover, it should be noted that only a small piece of membrane material (sections/details) was taken for the rejection measurements. Furthermore, both membrane modules were blocked with sludge several times due to sludge accumulating between the membrane pockets as a result of plant interruption. A dismounting was necessary to remove the blocked membrane pockets mechanically. Hence, this could have lead to minor membrane damages.

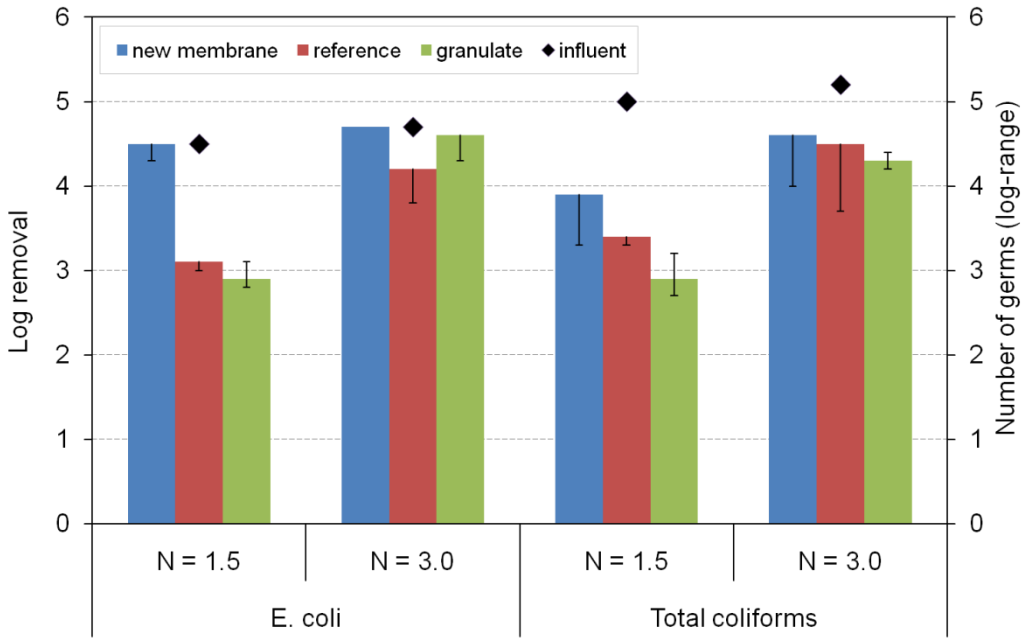


Figure 6-36: Mean values of Escherichia coli and coliform bacteria in the influent and log removal of the bacteria for a new membrane, reference, and membrane operated with granulate. The results represent mean values of two determinations per test sample. "N"– accumulation factor.

6.4.2.3. Effluent quality

For a continuous monitoring of the membranes' functioning, COD concentration and turbidity in the effluent of the lines holding granulate were measured during the whole test period. The COD concentration in the effluent of the MBR pilot plant - operated with synthetic wastewater - was 12.7 mg O_2/L ± 9.5 (test phase I). The turbidity of the effluent of line#2 in the MBR pilot plant was 0.09 NTU ± 0.08 on average, while the COD was 17 mg O_2/L ± 12.3. The average COD removal for this plant was about 95 % ± 3.4 (test phase II).

The effluent of the MBR pilot plant (C) in Wiesbaden-Biebrich - operated with real wastewater - showed turbidity values of about 0.26 NTU ± 0.12, while the COD was 18 mg O_2/L ± 4.7. Here, the average COD removal was about 95 % ± 1.3.

Over the whole test period, the results did not show any changes in the effluent quality of both plants holding granulate, thus indicating a constantly high removal of suspended solids and intact membrane conditions.

6.4.3. Change in ambient conditions (aerobic/anaerobic)

The investigation involved a change in milieu to be realized by changing the crossflow aeration system from air to nitrogen only in the filtration tank (line#3) between the 297th and the 398th day of operation. The tests were carried out at three different settings (1 h N_2, 1 h O_2; 24 h N_2, 24 h O_2; 48 h N_2, 48 h O_2). The change in milieu occurred very fast as a result of high oxygen consumption due to high concentrations of MLSS. The cyclic milieu change, i.e. from aerobic to anaerobic and vice versa, should lead to biofilm removal or at least stopping its buildup on the membrane surface.

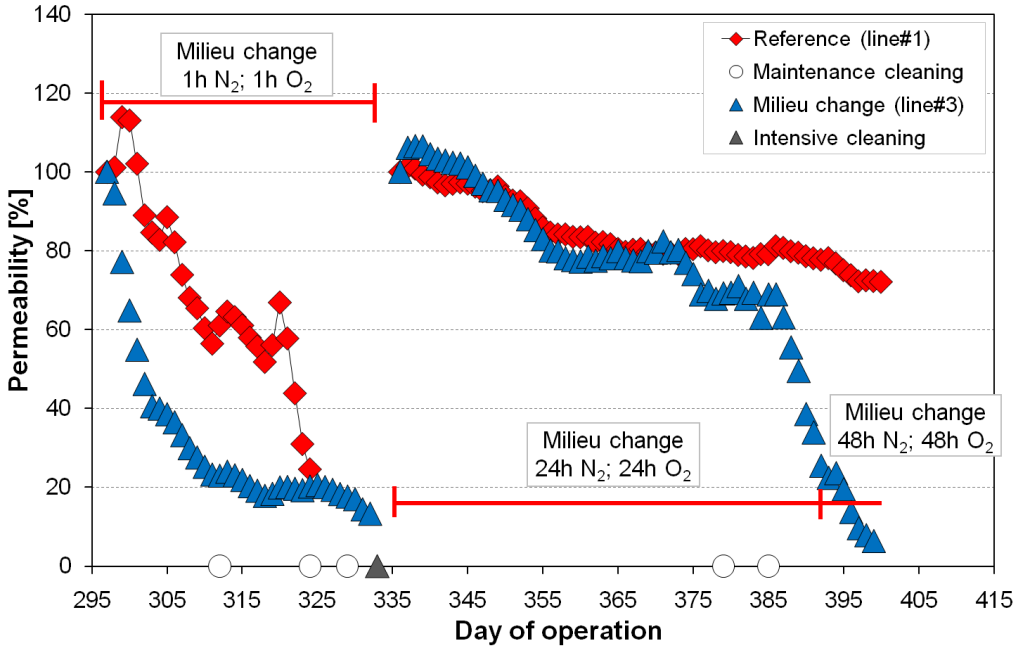


Figure 6-37: Trend of permeability for reference (line#1) and milieu change (line#3) in the MBR pilot plant (B). The permeability was normalized to 20 °C.

The permeability of the membrane module with the change in milieu declined significantly at an early stage of the first setting ((1 h N_2, 1 h O_2) and was recovered after intensive cleaning overnight with NaOCl (1,000 ppm) and citric acid (2 %) (see *Figure 6-37*). The trend of permeability of the reference module was similar in that operating phase. Both membrane modules were operated at a flux of 16 L/(m^2·h).

The second setting (24 h N_2, 24 h O_2) showed a fairly parallel course of the permeability of both lines until the 385th day of operation. However, the permeability of the module with milieu change decreased sharply starting from the 386th day, whereas the permeability of the reference line stayed more or less constant. The second and third setting were performed at a flux of 20 L/(m^2·h).

The results show that during the tests with a change in milieu conditions (aerobic, anaerobic) the biofilm layer that had built up on the membrane surface or membrane fouling due to pore blockage probably as a result of biopolymers retention (see *Table 6-9*) were not removed.

Table 6-9: DOC_{total} and DOC of biopolymers of 0.45 µm filtered samples (supernatant) and permeate taken on the 365th and the 379th day of operation.

Sample	DOC_{total} [mg/L]	DOC of biopolymers [mg/L]	DOC of biopolymers [%]
The 365th day of operation			
Supernatant - reference	5.02	1.00	19.9
Permeate - reference	2.82	0.06	2.1
Supernatant - milieu change	4.24	0.90	21.2
Permeate - milieu change	3.32	0.15	4.5
The 379th day of operation			
Supernatant - reference	6.90	1.75	25.4
Permeate - reference	5.07	0.08	1.6
Supernatant - milieu change	7.67	1.80	23.5
Permeate - milieu change	5.17	0.11	2.1

The activated sludge supernatant of both lines (milieu change and reference) is composed of up to 25 % (DOC) from biopolymers and up to 75 % (DOC) from humic substances and low molecular fractions (organic acids, and neutral substances). As the UV detection (see *Appendix B.4*) also showed a peak at the respective retention time, it is possible that the detected biopolymers (DOC) consist of proteins, at least to some extent.

Thus, the main difference among the investigated samples were the biopolymers, which were detected in the supernatant samples of both lines (milieu change and reference) operated in parallel. Biopolymers > 0.04 μm, which were rejected by the membranes, might cause a decline in the permeability of these lines.

6.4.4. Backwash with a salt brine solution

The backwash with a salt brine solution between 1 % and 3 % was investigated at the MBR plant (A) in Darmstadt-Eberstadt in order to provide information on the effect of cleaning clogged membrane pores. The test conditions, i.e. backwash duration (= contact time of the brine solution with the membrane), air flow rate of the fine-bubble crossflow system, and the flux rate were kept constant during the experimental period.

In *Figure 6-38,* the trend of permeability (temperature corrected to 20 °C) and the backwash with the brine solution marked at specified concentrations is illustrated. The MBR plant was operated at a flux of 14.4 L/(m^2·h) ± 0.6.

Following the principle that a salt solution holds free charge carriers that shield the monomer charge weakening electrical interaction, the change in electrolyte concentrations was meant to remobilize ionogenic macromolecules that clog the membrane pores, allowing the blocked pores to be rinsed free.

The results show that the brine solution had no positive impact on membrane performance. During the initial stage of the experiments, after the use of 1 % brine solution, an increase in permeability was observed, however the concentration of colloidal matter in the supernatant changed at the same time. Moreover, the use of higher concentrations of brine solution (2 % and 3 %) showed no positive results. Thereupon, the experiments were not continued.

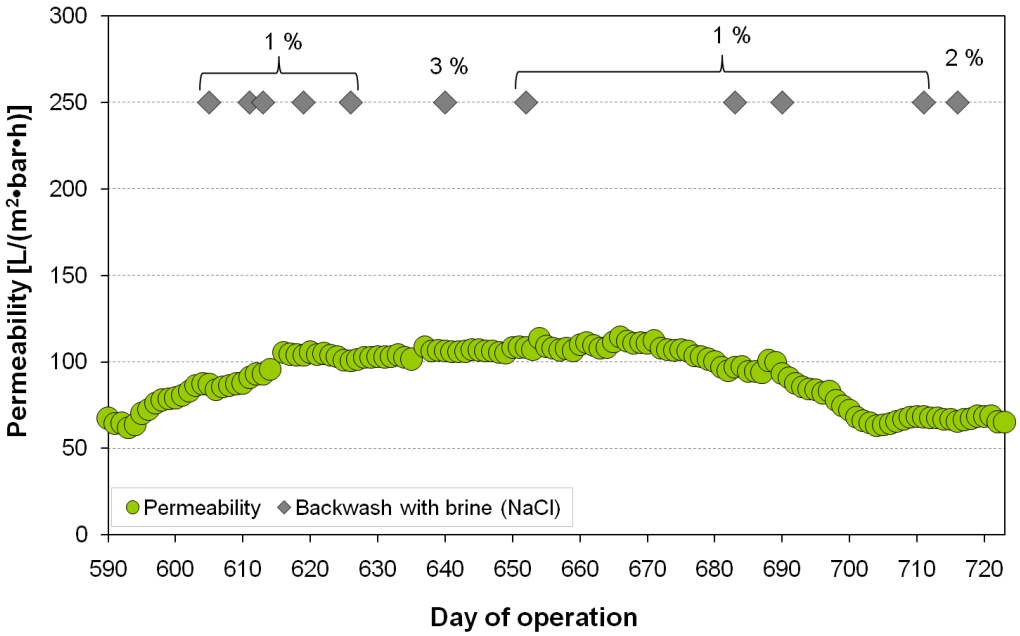


Figure 6-38: Membrane backwash with a salt brine solution at the MBR plant (A) in Darmstadt-Eberstadt. The permeability was normalized to 20 °C.

6.4.5. Chemical cleaning

Membrane cleaning is an integral part in the operation of ultrafiltration systems in MBRs and has a significant impact on process operations. In order to remove the fouling layer and keep membrane pores free of clogging, the following combination of methods was implemented at the MBR pilot plant (B) in Wiesbaden-Biebrich and at the MBR plant (A) in Darmstadt-Eberstadt. First, the cake layer was removed from the membrane surface using the fine-bubble crossflow system that was installed beneath the membrane module and that operated continuously. Secondly, the membrane modules were operated with cyclic backwash and relaxation intervals.

In addition, maintenance cleanings were performed approximately weekly using sodium hypochlorite (200 ppm for the MBR plant (A); 500÷1,000 ppm for the MBR pilot plant (B)). The maintenance chemical cleaning (in-situ) was carried out directly in the permeate tanks, to which the chemicals were added. Membranes were rinsed with chemicals about 20 minutes from the inside outwards via backwash procedure. *Figure 6-39* shows the trend of permeability and maintenance cleanings applied during the operational period. The MBR plant (A) was operated at a flux of 14.4 L/(m^2·h) ± 0.6.

The objective of chemical cleaning is to remove “irreversible” fouling that accumulates during the filtration step and thus to prevent a sharp decline in membrane performance. It can be seen that preventive maintenance cleaning did not cause any significant increase in permeability. Despite chemical cleaning, the permeability even declined. This might be due to the cake layer formation rather than a consequence of pore blockage. Mass transfer barriers within the fouling layer are likely to be the rate-limiting factor for chemical maintenance cleaning.

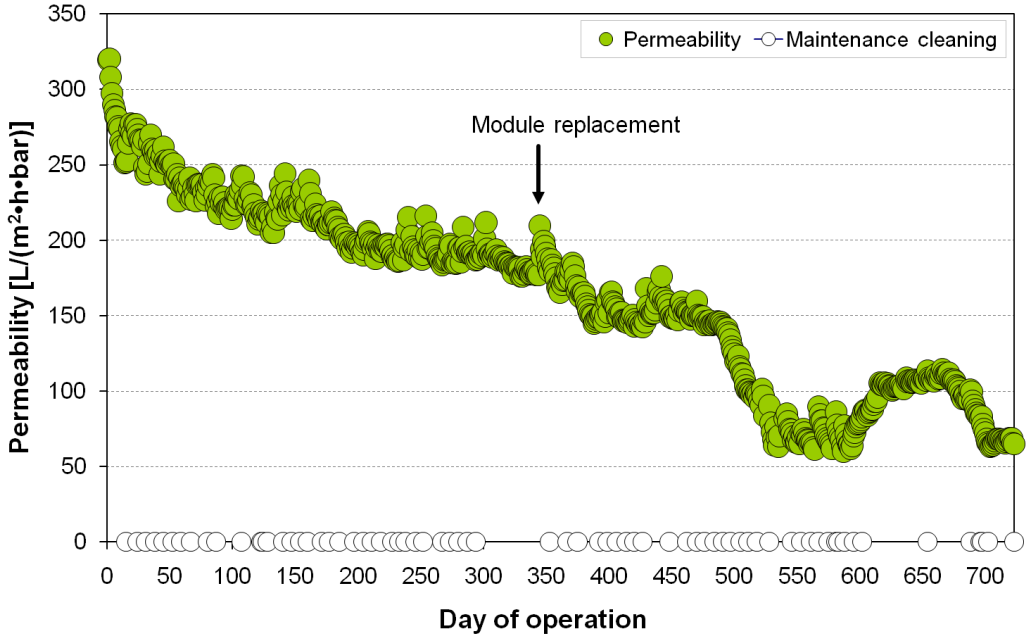


Figure 6-39: Chemical cleaning of membrane at the MBR plant (A) in Darmstadt-Eberstadt. The permeability was normalized to 20 °C.

The cleaning strategy of the reference module (line#1) at the MBR pilot plant (B) in Wiesbaden-Biebrich is based on regular (weekly) maintenance cleanings and occasional intensive cleanings, the latter on the 333rd day and the 568th day, using sodium hypochlorite (1,000÷1,500 ppm) and citric acid (2 %) over 24 hours minimum. The membrane was operated at different flux rates.

Figure 6-40 shows that the intensive cleanings contributed to the jump in permeability to values > 600 L/(m^2·h·bar), however, the maintenance cleaning did not significantly improve the permeability. On the 114th day of operation, the effect of mechanical cleaning by granulate was tested (see *chapter 6.4.1.4*). As a result, the permeability of the "blocked" reference membrane was recovered and an almost five-fold increase in permeability within one week was observed. Hence, intensive cleaning shows similar results as mechanical cleaning. On the 449th day of operation, the MBR pilot plant (B) was re-inoculated with fresh activated sludge (ca. 0.74 m^3) from a MBR plant of Microdyn-Nadir because of a malfunction, resulting in the total loss of activated sludge. This action led to a significant increase in permeability of the reference membrane.

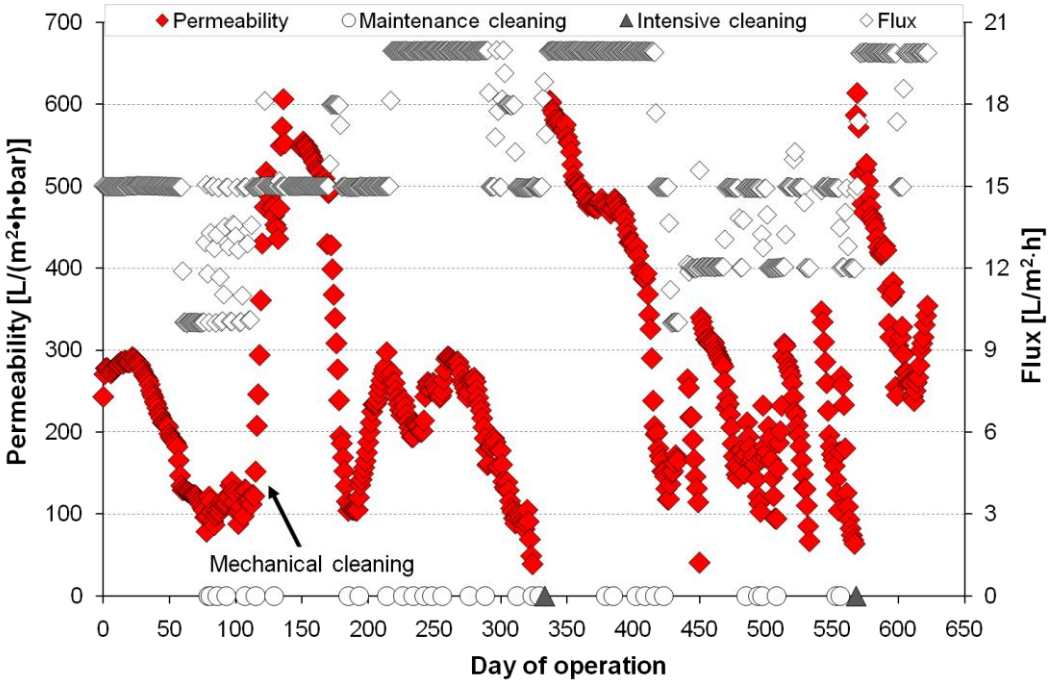


Figure 6-40: Chemical cleaning of the reference line#1 at the MBR pilot plant (B) in Wiesbaden-Biebrich. The permeability was normalized to 20 °C.

6.4.6. Long-term relaxation

Relaxation intervals are applied by shutting down the permeate flow. They are used to control the cake layer formation of membranes and to extend the intervals between maintenance cleanings. During the relaxation mode, the membranes return to their original relaxed state, as membranes are basically elastic in nature. The days being out of operation due to malfunctions or maintenance works are called long-term relaxation intervals. During relaxation, the aeration of the membrane at the MBR plant (A) in Darmstadt-Eberstadt stayed in operating mode in order to assist the renewal of biomass solids in the vicinity of the membrane surface.

Figure 6-41 represents the long-term relaxation intervals of membrane. The results show that the permeability recovered in these days. This means that extended relaxation intervals could alleviate membrane fouling and thus have a positive effect on membrane performance. However, relaxation breaks involve high specific costs due to operation interruptions i.e. low membrane throughput, which directly translates to bigger membrane area.

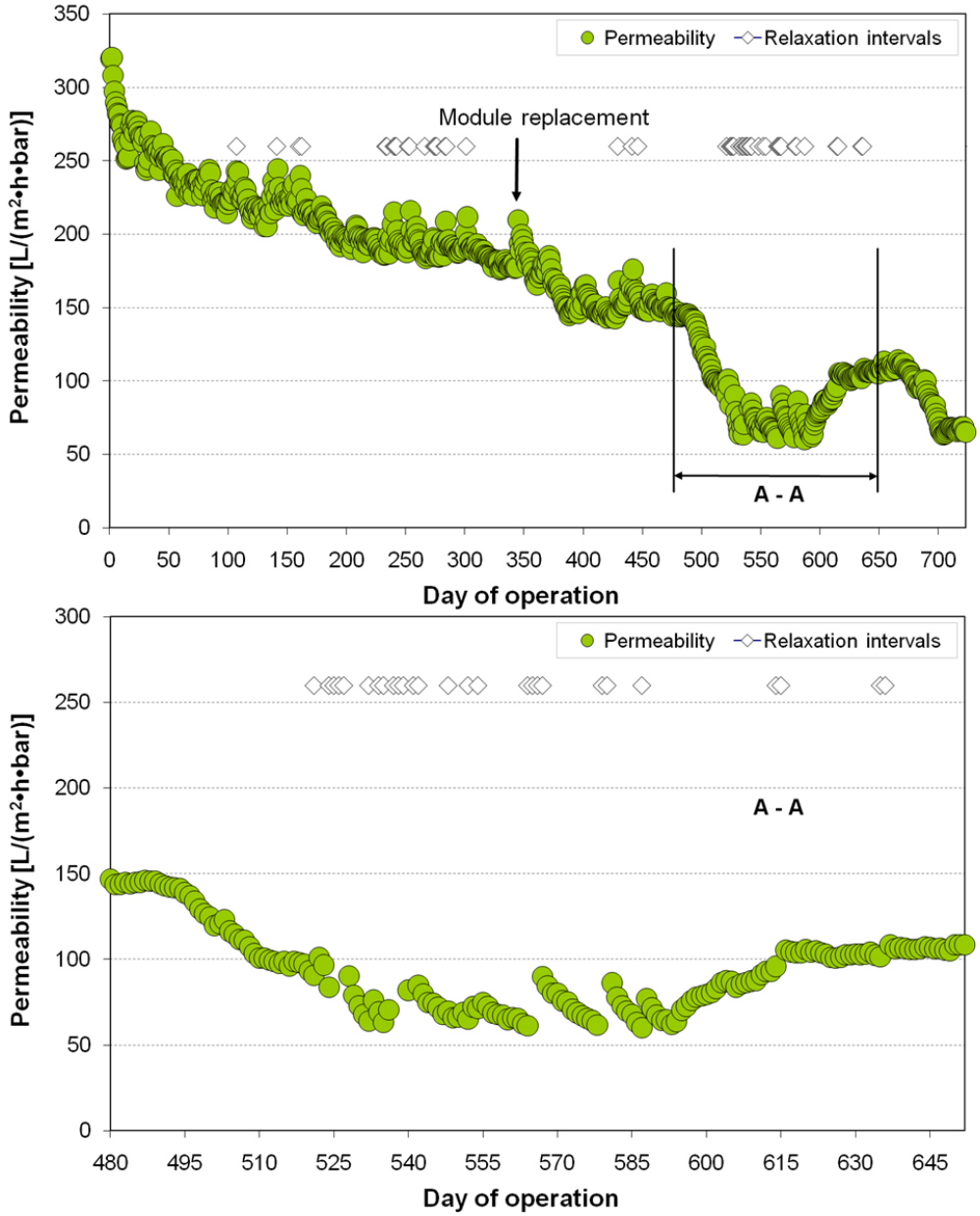


Figure 6-41: Relaxation intervals of the membrane at the MBR plant (A) in Darmstadt-Eberstadt over the whole investigation period a), and between the 480th and the 652nd day of operation b). The permeability was normalized to 20 °C.

6.4.7. Crossflow aeration system

6.4.7.1. Efficiency

Clean water tests on oxygen transfer were performed with the fine-bubble and coarse-bubble crossflow aeration system at different air volume rates (20 m^3/h, 40 m^3/h, 60 m^3/h, and 80 m^3/h) for the optimization of the crossflow aeration system with regard to the energy demand. The specific aeration demand per membrane area SAD_m was between 0.21 and 0.62 $m^3_N/(m^2_A \cdot h)$.

The results of oxygen transfer measurements are gathered in *Table 6-10* and *Table 6-11*. The individual measurements include: air flow rate - Q_L - (m^3/h or specific in $m^3/(m^3_{BB} \cdot h)$ and $m^3/(m^2_A \cdot h)$ at STP), apparent volumetric mass transfer coefficient at 20 °C (k_La_{20}), oxygen transfer rate OTR (kg O_2/h or

specific SOTR in g/(m^3·m) at STP), standard oxygen transfer efficiency – SOTE - (% or specific %/m), and standard aeration efficiency - SAE_{gross} - (kg O_2/kWh).

Table 6-10: Oxygen transfer rates with the fine-bubble crossflow aeration system.

Test No	Q_L			k_La_{20}	SOTR	SSOTR	SSOTE	SAE
	[m^3_N/h]	[m^3_N/m^3_{BB}·h]	[m^3_N/m^2_A·h]	[1/h]	[kg O_2/h]	[g/m^3_N·m]	[%/m]	[kg O_2/kWh]
1	21.43	7.14	0.21	23.96	0.71	18.7	6.25	4.16
2	39.67	13.22	0.4	47.72	1.41	20.1	6.73	4.47
3	62.02	20.67	0.62	71.40	2.11	19.25	6.44	4.28

Table 6-11: Oxygen transfer rates with the coarse-bubble crossflow aeration system.

Test No	Q_L			k_La_{20}	SOTR	SSOTR	SSOTE	SAE
	[m^3_N/h]	[m^3_N/m^3_{BB}·h]	[m^3_N/m^2_A·h]	[1/h]	[kg O_2/h]	[g/m^3_N·m]	[%/m]	[kg O_2/kWh]
1	20.23	6.7	0.20	9.61	0.28	9.6	3.2	2.12
2	40.51	13.5	0.41	20.00	0.58	9.9	3.32	2.21
3	58.35	19.5	0.58	29.87	0.87	10.3	3.44	2.29
4	82.52	27.5	0.83	40.71	1.19	9.9	3.32	2.21

Figure 6-42 presents specific standard oxygen transfer rates in dependence of specific air flow rates. The oxygen transfer rate is independent of the specific air flow rate in the investigated range. The fine-bubble crossflow aeration system could enter 20.1 g O_2/(m^3·m) into clean water at a specific air flow rate of 13.22 m^3/(m^3_{tank}·h) or 0.4 m^3/(m^2_A·h). In contrast, the coarse-bubble crossflow system only achieved oxygen transfer rates of 9.9 g O_2/(m^3·m) at a specific air flow rate of 13.5 m^3/(m^3_{tank}·h) or 0.41 m^3/(m^2_A·h).

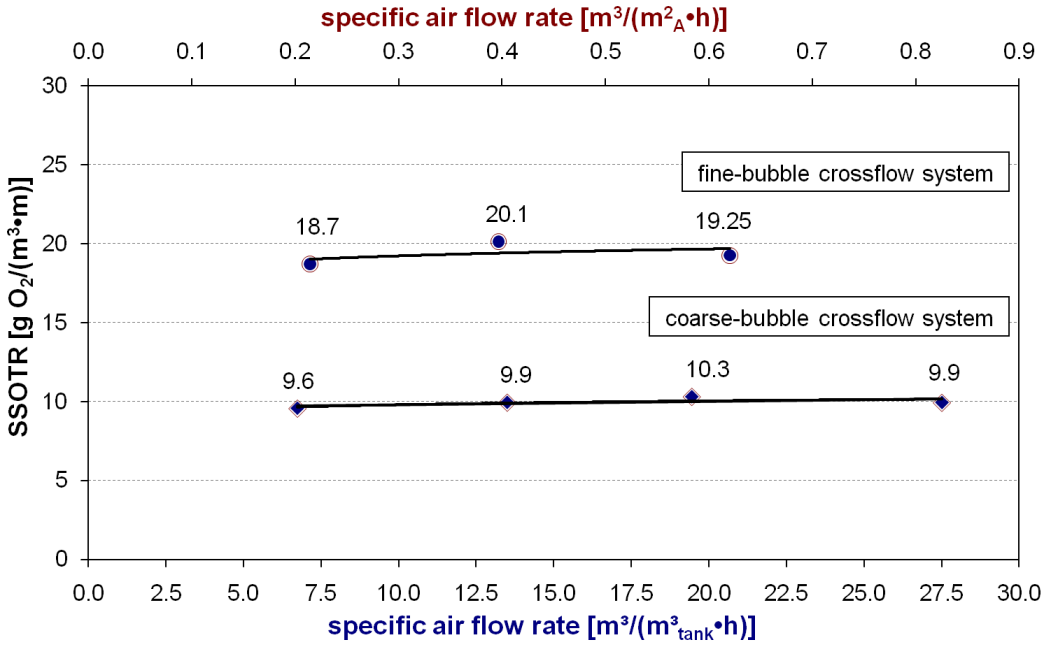


Figure 6-42: Specific standard oxygen transfer rates in dependence of specific air flow rates, related to the volume of the tank or the membrane area.

In *Figure 6-43,* the specific standard oxygen transfer efficiency (SSOTE) vs. specific air flow rates is illustrated. The term "standard oxygen transfer efficiency" is generally understood to describe the percentage of the mass of oxygen in an injected air stream dissolved into clean water at STP (standard temperature pressure conditions). The oxygen transfer efficiency - among many others variables - depends heavily on the coverage (surface) density of the aeration system in the aeration tank concerned.

In this case, the coverage density for the fine-bubble and coarse-bubble crossflow system is 38 % and 41 %, respectively. The specific standard oxygen transfer efficiency for the fine-bubble crossflow system is in the range of 6.25 to 6.73 %/m, whereas SSOTE for coarse-bubble crossflow system was measured as low as 3.20 to 3.44 %/m.

According to a modified table of standards for compressed aeration systems, *Wagner (2001)* specifies SSOTEs between 6 and 8 %/m (for middle to more favorable range) in clean water for area-wide fine-bubble aeration elements. These values were achieved with the existing fine-bubble crossflow system for the middle range. Hence, high rates of the oxygen transfer efficiency were measured as a result of intensive mixing of the tank and due to the fine distribution of air bubbles.

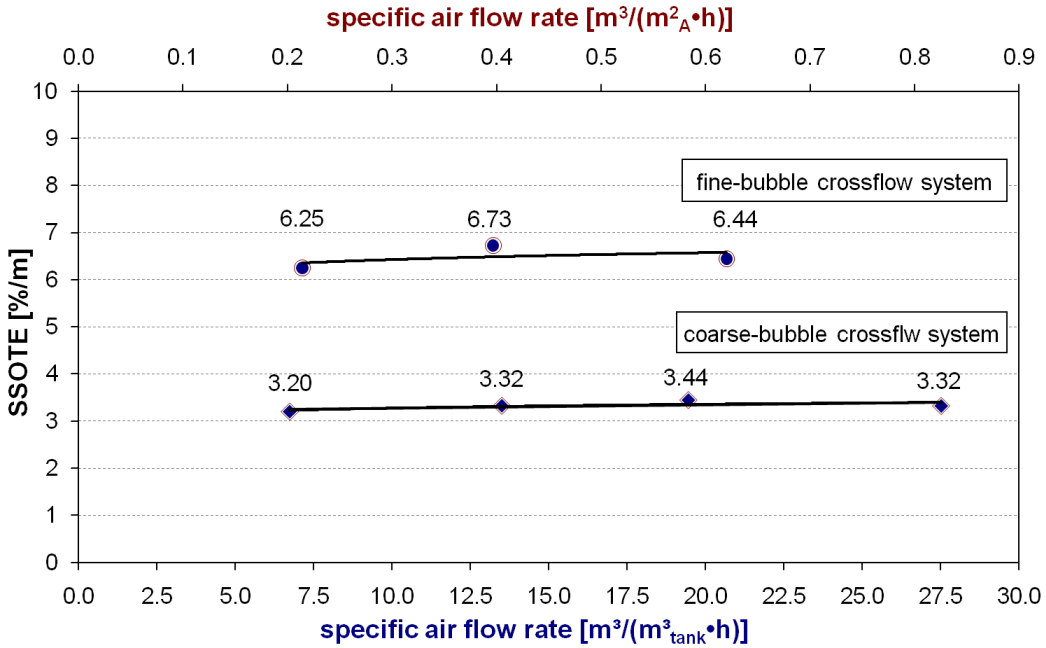


Figure 6-43: Specific standard oxygen transfer efficiency vs. specific air flow rate, related to the volume of the tank or the membrane area.

The assessment of the efficiency of aeration systems is made via aeration efficiency SAE (kg O_2/kWh). *Figure 6-44* shows standard aeration efficiency rates vs. specific air flow rates for the fine-bubble and coarse-bubble crossflow system. In order to calculate the gross rate of the oxygen transfer efficiency, a compressor performance was normalized with practice-oriented efficiency factors (compressor: $\eta = 0.6$).

According to the above-mentioned table of standards (*Wagner, 2001*), oxygen transfer efficiency rates were found to be between 3.4 and 4.5 kg O_2/kWh. The SAE values (between 4.16 and 4.47 kg O_2/kWh) that were measured for the fine-bubble crossflow system, matched the modified table of standards. In contrast, the results for the coarse-bubble crossflow system show - as expected - lower SAEs that are in a range of 2.12 and 2.29 kg O_2/kWh. The energy consumption of the coarse-bubble crossflow system for fouling control is about two times higher than the fine-bubble crossflow system for oxygen supply.

Cornel et al. (2002) investigated oxygen transfer rates for coarse and fine-bubble crossflow systems under real conditions and they concluded that coarse-bubbles applied for membrane scouring are three times less efficient in oxygen transfer than fine-bubbles. The difference between the energy consumption of coarse and fine-bubble crossflow systems as reported by *Cornel at al. (2002)* and the values measured in this thesis results from the difference in measured media and the variations of specific air flow rates and immersion depth of diffuser for different manufacturers of membrane systems.

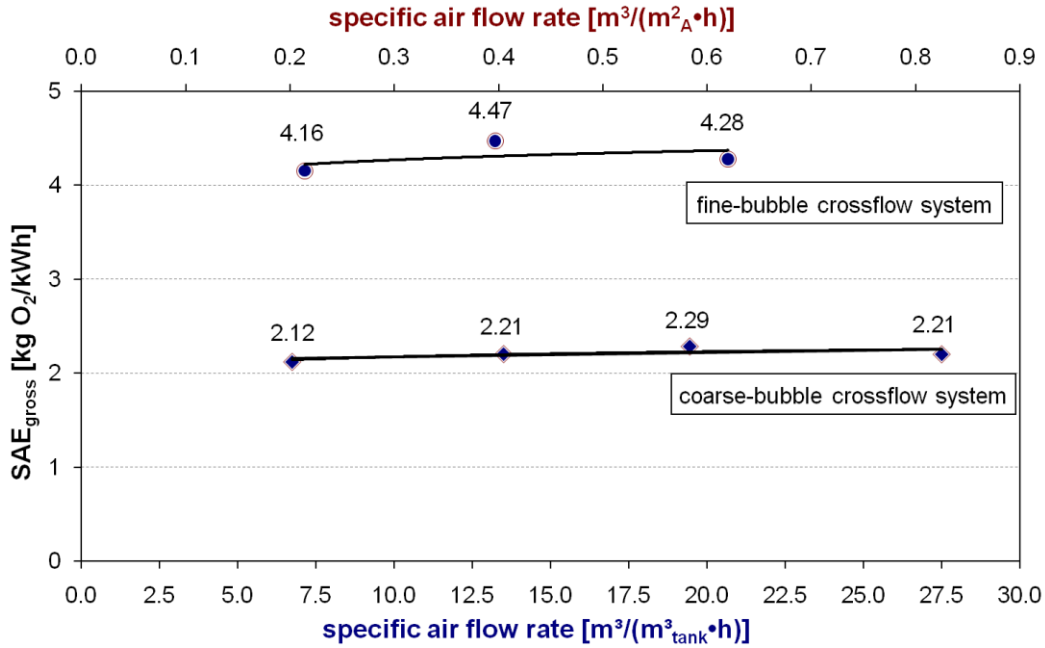


Figure 6-44: Standard aeration efficiency vs. specific air flow rate, related to the volume of the tank or the membrane area.

7. Economic feasibility of mechanical cleaning

Membranes represent a relevant capital cost factor. That is to say, all factors that reduce the membranes' lifetime and/or the membrane flux will directly affect the economic feasibility of the MBR process. In principle, the following savings can be achieved via the reduction of membrane fouling using mechanical cleaning by granulate.

7.1. Increase of membrane throughput/flux (without chemical cleaning)

The objective of mechanical cleaning by granulate is to reduce membrane fouling by abrasion, thereby increasing the membrane throughput. Granulate continuously rub against the membrane surface and thereby prevent not only the deposition of fouling layers, but also remove the material that has already been deposited.

It was observed that granulate causes self-cleaning of the membrane. This is important from the point of view of saving on chemical cleaning agents and increasing the operation time. Granulate proved to be very effective, as the membrane throughput increased by about 27 % compared to the reference membrane.

Achieving higher flux rates/membrane throughput with granulate, directly translates to less membrane area and thus lower capital and maintenance cost, as less energy for the aeration crossflow system is needed. According to *Yoon and Collins (2006)*, the savings in membrane application can be calculated using the following equation:

$$\text{Savings (\%)} = (\text{flux increase (\%)}/(100 + \text{flux increase (\%)})) \times 100 \quad (7.1)$$

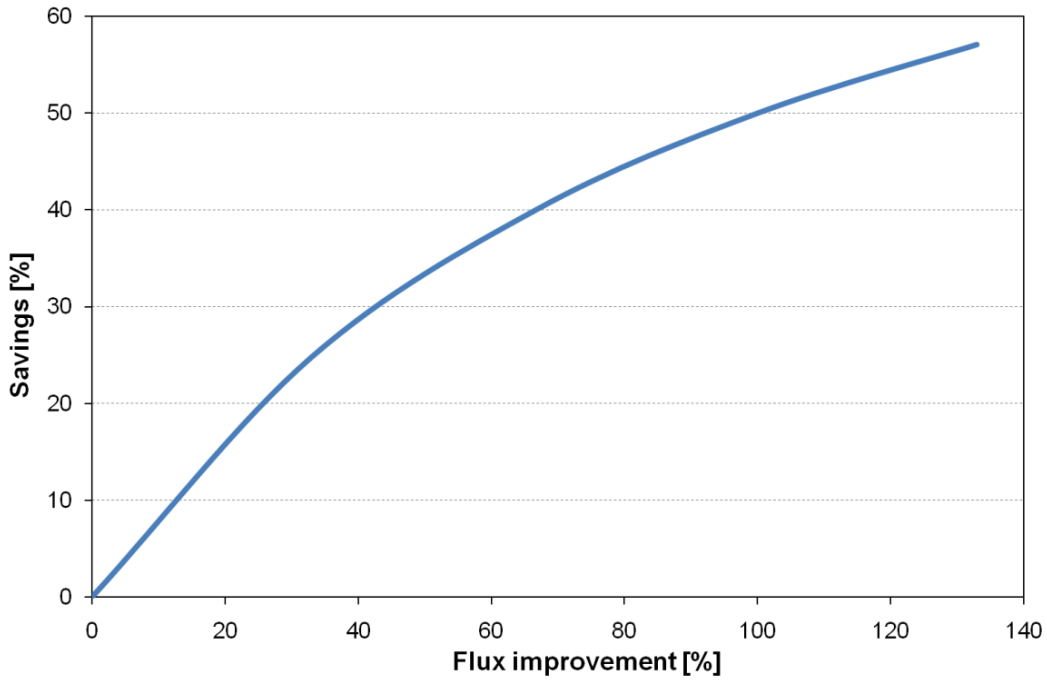


Figure 7-1: Savings due to flux improvement for the MBR pilot plant (B) in Wiesbaden-Biebrich.

Figure 7-1 shows that by using granulate, up to 60 % of costs can be saved due to achieving higher flux rates up to 135 % (35 L/(m^2·h)) compared to the reference membrane (15 L/(m^2·h)).

7.2. Cost reduction for membrane cleaning

Chemical cleaning to maintain membrane performance can be omitted via the use of mechanical cleaning by granulate. Accordingly, costs for chemicals, manpower, and the disposal of residual chemical solutions can be saved. In addition, the mechanical strength of polymer membranes is not affected by chemical cleaning solutions (hypochlorite), hence significantly minimizing the membrane aging. *Arkhangelsky et al. (2007)* report on the degradation of UF membranes exposed to in-place chemical cleaning. Washout of copolymers in membrane skin layer and the permanent change of functional groups at the membrane surface lead to membrane aging. Thereby, omitting membrane cleaning can result in extended lifetimes of UF membranes. Moreover, membrane cleaning activities directly affect reactor operation due to the need for process interruptions.

Costs arising from the operation with granulate:

- The cost for granulate is approximately 0.08 €/m^2 (1.5 €/kg) considering 2.6 kg granulate/m^3_{tank} for a membrane with an area of 50 m^2. Assuming a lifetime of approximately 2 years for the granulate, annual costs are 0.04 €/(m^2·a).
  Under working conditions, the granular material selected for the experiments showed good resistance to cyclic variations in temperature, load, moisture content, and the chemical environment, not being affected by the chemical properties of the liquid to be treated. The selection of suitable, durable and long-living granular material is essential for cost efficiency.
- Any breakdown of the material would change the smooth surface of the granular material, thus increasing the risk of membrane damage. In case of membrane damage, the specific membrane costs are approximately 60-70 €/m^2 (*Pinnekamp et al., 2006*). However, as mentioned above, UF membranes can be equally damaged as a result of chemical cleaning. As MBR plants have been in operation for some time and experience has been gained, membrane lifetimes appear to be longer than initially expected. The first continuously operated full-scale municipal MBR plant in Europe, at the WWTP in Porlock (UK) has been commissioned in 1998. *Churchouse et al. (2008)* report that given the remarkably low failure rates, any overhaul until year 12 or later is not anticipated.
- To retain granulate inside the membrane tank it is necessary to install a screen with 1 mm pore size.

Savings resulting from the operation with granulate:

- Via the operation with granulate, about 27 % higher membrane throughputs are achieved compared to the reference membrane.
- Higher membrane throughputs result in less membrane area and thus lower capital and maintenance cost, as less energy for the aeration crossflow system, which is between 0.5-1.2 kWh/m^3 permeate according to *DWA (2007)*, is needed.
- Costs for chemical cleaning can be reduced, which is approximately 0.22-1.1 €/(m^2·a) (*Wedi, 2005*).
- Manpower costs can be reduced as no chemical cleaning is needed. According to *Reicherter (2003)*, manpower costs for a municipal WWTP are about 15-40 % of operating costs.

- Sustainable operation with minimized environmental impacts is possible (no chemical by-products such as AOX due to the use of NaOCl).

It is apparent that mechanical cleaning via granulate is far more economical and sustainable in comparison to a conventional MBR.

8. Final conclusions

From the above-mentioned experiments the following conclusions can be summarized:

- **The impact of sludge characteristics and operating conditions on membrane fouling**

SRT, sludge loading, colloidal matter, viscosity, MLSS content, wastewater and sludge composition, as well as the operating temperature affect the permeability of membranes. Some parameters are closely related and cannot be varied independently of each other.

A colloidal fraction (0.45-0.04 μm) was identified by comparing the results of the COD measurements in the supernatant of activated sludge $COD_{0.45\,\mu m}$ and in the permeate $COD_{0.04\,\mu m}$, the colloidal fraction ($COD_{colloidal}$). The concentration of this colloidal fraction obviously depends on the operating temperature and SRT. $COD_{colloidal}$ concentration seems to increase at lower temperatures.

Parallel measurements of proteins and polysaccharides concentration prove a nearly linear correlation with the colloidal fraction ($COD_{colloidal}$). However, while a relationship between the retention of biopolymers (proteins and polysaccharides) and the CST of activated sludge was found, a clear connection with the permeability of the investigated membranes does not exist.

For a reliable description of fouling phenomena, a combination of several factors has to be considered, i.e. not only biopolymers amounts, but also physicochemical parameters in the system (temperature, SRT) as well as membrane characteristics.

The addition of polyaluminum chloride coagulant resulted in the reduction of the colloidal fraction in the supernatant by up to 80 % of the initial value. The coagulant even bound soluble matter $< 0.04\,\mu$m, as COD concentrations of permeate were slightly higher.

Fractionation tests showed that the fraction 0.04-0.1 μm constituted the largest percentage of COD (71 %) and DOC (81 %) of samples during high fouling in the MBR, whereas during low fouling made up only 21 % (COD) and 20 % (DOC). It was observed that biological degradation of organic matter was much higher during periods of low fouling. Only 41 % of organic compounds were retained by the membrane in the reactor compared to 84 % during periods of high fouling. Moreover, this implies that most of the biopolymers (proteins, polysaccharides) were retained in the reactor by membrane separation.

It was found that the truly soluble matter ($< 0.04\,\mu$m) seems to affect membrane fouling only to a minor degree. Although both lines were operated at the same flux, there was only a slight permeability decrease in the downstream line#3, while the permeability of reference line#1 showed a significant decline despite chemical cleaning. Thus, the decline of permeability of reference line#1 was caused predominantly by colloids and/or particles $> 0.04\,\mu$m.

The effect of enhanced water flux on the fouling potential of the membrane module operated in sequence was not clear. Although a decline in the membrane permeability of the line operated in sequence (line#3) was observed it is not clear whether the permeability decrease was caused by the increase in the flux rate or the effluent composition of line#2 (upstream stage).

The chromatographical analysis using gel permeation chromatography (LC-OCD) showed that the main difference among the investigated samples were the biopolymers, which were detected only in the supernatant of the upstream line. Thus, biopolymers $> 0.04\,\mu$m, which were rejected by the upstream membranes, could cause a decline in the permeability of these lines.

It is to be considered, however, that all changes in upstream lines could have a direct impact on the permeability performance of line#3 because of the operation in sequence, i.e. changes in the influent composition, flux or MLSS content, but also the chemical cleaning procedure of reference line#1.

The rheological measurements showed a structural viscous behavior of the investigated activated sludge samples, i.e. sludge viscosity decreases with increasing shear rate. Moreover, it was found that with increasing MLSS concentration, the viscosity tends also to increase. The viscosity amounts to 18 mPa·s at a "common" MLSS concentration of 12 g/L in MBRs and the shear rate of 40 s^{-1}.

Additionally, a correlation between the apparent viscosity and the retention of proteins and polysaccharides in the mixed liquor filtrate of activated sludge was observed.

All measured data were interpreted both with the approach of Oswald de Waele (structural viscous behavior without yield stress) and Herschel-Bulkley (flow curve with apparent yield stress). The coefficients of both model approaches can be described as a function of MLSS concentration using a non-linear regression analysis. The Oswald de Waele approach showed a better plausibility with the measures values.

Microbiological analyses of activated sludge at different SRTs showed that there are constant changes in the microbial community during the subsequent operation.

The experimental periods between the 97th and the 114th day, and the 430th and 557th day were interrupted due to the appearance of filamentous bacteria. Enormous foaming and bulking led to process instability that was reflected in the increased occurrence of attached ciliates. One of the reasons for the dominancy of filamentous microorganisms was the introduction of paper mill wastewater, creating an atypical composition of the influent wastewater with high concentrations of surfactants.

- **Application of mechanical cleaning with granular material**

The application of mechanical cleaning by granulate (inert, inorganic material) supported by crossflow system was investigated in order to remove and minimize the formation of fouling layers by abrasion, thereby increasing the membrane throughput. Experiments were carried out for municipal and synthetic wastewater. The granulate continuously prevent not only deposition of fouling layer, but also remove material that has already been deposited on the membrane surface, making it possible to operate a MBR long-term and continuously.

The investigations proved to be extremely successful as described below.

Test phase I

In preliminary investigations on the selection of granular material at the MBR pilot plant reference line and two granulate lines (TPU ρ = 1.2 kg/L, ϕ = 3.5 mm; PMMA ρ = 1.18 kg/L, ϕ = 2.5 mm) were operated in parallel. The most appropriate SAD_m for the granular material to be moved into the loop was 0.7 $m^3/(m^2 \cdot h)$. During six weeks of operation, the cleaning performance of granulate was investigated at flux rates between 10-15 $L/(m^2 \cdot h)$ and compared with the reference line.

It was observed that as long as granulate circulated in the filtration tanks, the permeability stayed at a high level, whereas the permeability of the reference module sharply decreased (90 % of the initial value) within one month of operation. Despite chemical cleaning of the reference module, the permeability decreased. As a result of granulate settling, the permeability of the membrane operated with PMMA granulate declined significantly, therefore lighter granulates were chosen for further tests.

The results show that granulate demonstrated a positive effect on the permeability. Moreover, during the whole test period, chemical cleaning was not necessary for both membrane modules operated with granulate.

One of the main problems concerned with the use of granulate in MBRs is the risk of the membrane damage due to continuous bombardment. SEM images of the surface of membranes operated with TPU and PMMA granulate clearly showed scratches and folds after 43 days of operation due to granulate collisions. The membrane operated with TPU granulate seems to be more damaged than that operated with PMMA. As TPU granulates are slightly larger and heavier it can be concluded that the risk of membrane damage increases with increasing granulate size or density. However, the visual marks do not necessarily indicate membrane damage.

Rejection measurements of membranes operated with TPU and PMMA granulate showed that these membranes were slightly damaged due to abrasive effects. The rejection measurements for the membrane cleaned with TPU granulate showed significantly worse results (49.6 % ± 19.2) than for PMMA granulate (69.8 % ± 27.7), whereas the rejection measurements of the reference membrane were similar to a new membrane (> 90 %).

Over the whole test period, COD concentration and turbidity did not show any negative changes in the effluent of both plants holding granulate, thus indicating a constantly high removal of suspended solids and intact membrane conditions.

Test phase II

Following the success of the preliminary tests, further experiments with granulate were performed over a long time period of more than 600 days. Reference line#1 (without granulate) and line#2 with PPTV20 granulate (ρ = 1.05 kg/L, ϕ = 2.5 mm) were operated in parallel with synthetic wastewater in long-term experiments.

The initial permeability stayed more or less constant at a flux of 15-35 L/(m^2·h); however, as a result of increasing the flux from 35 up to 40 L/(m^2·h) the permeability declined significantly. During further operation, the initial permeability did not recover, even after decreasing the flux level again. It seems that MBR operation at high flux rates of 35-40 L/(m^2·h) leads to irreversible fouling inside the membrane pores, which cannot be removed by granulate. This might be caused by permeation drag force.

Furthermore, as a result of short-term addition of PPTV20 granulate into the reference line a 5-fold increase in permeability was observed within only one week. The “blocked” reference membrane was restored probably due to abrasion of deposits on the membrane surface.

During the whole experimental period of 622 days of continuous operation, no chemical cleaning in the granulate holding line#2 was carried out, whereas the reference module was cleaned with chemical agents.

It was shown that granulate can greatly enhance the performance of ultrafiltration membranes as the flux rates increased considerably (over 27 %) compared to the reference line (without granulate), that showed a significant decline in permeability.

Thus, using granulate up to 60 % of the costs can be saved by achieving higher flux rates up to 135 % (35 L/(m^2·h) compared to the reference membrane (15 L/(m^2·h). Since the permeate flux/membrane throughput is an important factor from an economical point of view, being directly translated to less membrane area and automatically to less energy for aeration crossflow system, the application of granulate leads to a cost-reducing increase in membrane performance.

It was observed that granulate causes self-cleaning of the membrane, continuously removing deposits due to abrasive effects. This is important from the point of view of saving on chemical cleaning agents, manpower performing the cleaning, disposal of residual chemicals, and increasing the operating time.

The cost for granulate is approximately 0.08 €/m^2 (1.5 €/kg) considering 2.6 kg granulate/m^3_{tank} for a membrane with an area of 50 m^2. Assuming that the lifetime of granulate is approximately 2 years, annual costs are reduced to 0.04 €/(m^2·a). Thus, it is apparent that mechanical cleaning by granulate is far more economical and sustainable in comparison to a conventional MBR, as no chemicals are in use.

Moreover, it was demonstrated that the findings from MBR pilot plant (B) operation with synthetic wastewater could also be applied to real conditions (MBR plant C), as nearly constant permeability values at a flux between 10 and 14 L/(m^2·h) were observed over 100 days of operation. The MBR plant was operated at MLSS between 4 and 21 g/L and without any backwash with permeate, relaxation breaks or chemical cleaning. Thus, it is concluded that permanent mechanical cleaning by granulate prevents membrane fouling and permeability loss, which would have been expected for the operation without granulate.

However, during mechanical cleaning by granulate, there was a potential risk that not only the fouling layer on the membrane surface was removed but also the membrane material was damaged as a result of abrasive cleaning.

At the end of the experiments, the membranes were analyzed by SEM. Comparing the SEMs after 25 months of operation, it is obvious that the granular material left marks (folding and collision marks) on the membrane surface, whereas the reference membrane clearly showed a fairly smooth surface without any folding, although with one noticeable point mark.

As the images only show the surface condition of the membrane skin and do not disclose the condition of the porous structure of the membrane, integrity tests were performed in order to estimate the actual functioning of the membrane material.

The membrane of plant operated with synthetic wastewater, line#2 showed rejection rates of 89.9 % ± 3.4 after 25 months of operation. Thus, no damaging effects by granulate could be observed, as the rates were comparable with those of new membranes (95.1 ± 1.9). Moreover, the rejection rate of the reference membrane (87.4 ± 9.9) was even lower than that of the membrane operated with granulate.

The turbidity of the effluent of line#2 was 0.09 NTU ± 0.08 on average, while the COD was 17 mg O_2/L ± 12.3. The average COD removal for this plant was about 95 % ± 3.4.

In contrast, the rejection rates of the membranes used in the plant operated with real wastewater dropped significantly to 40 % ± 29; however, only a small piece of membrane material (sections/details) was taken for the rejection measurements.

All the same, the effluent quality (COD and turbidity) remained superior. Turbidity was about 0.26 NTU ± 0.12, while the COD was 18 mg O_2/L ± 4.7. Here, the average COD removal was about 95 % ± 1.3.

Over the whole test period, the results did not show any negative changes in the effluent quality of both plants holding granulate, thus indicating a constantly high removal of suspended solids and intact membrane conditions.

In order to control whether the membrane operated with granulate still rejected viable bacteria, integrity tests of microbial removal for the two common water-related bacteria indicators, viz. Escherichia coli and total coliforms, were conducted. Cutting wear of the membrane due to granulate could increase not only the rejection rates but also the number of bacteria in the sample.

The new membrane removed five (100 %) and four of six logs of Escherichia coli and total coliforms, respectively. The membranes operated with granulate and the reference line, which had rejection rates between 87.4 ± 9.9 and 89.9 % ± 3.4 %, with the test solution, showed bacteria removal of E. coli and total coliforms still to be 3 logs. These results indicate that the granulates did not have any negative impact on the membranes and still reject almost all bacteria in the system.

There were some bacteria detected in the effluent of all investigated membranes. However, this was probably due to microbial colonization of a section of the system piping rather than to bacterial penetration of the new membranes. Moreover, only a small piece of membrane material (sections/details) was taken for the rejection measurements and both membrane modules were blocked several times with sludge due to sludge accumulation between the membrane pockets as a result of plant interruption. A dismounting was necessary to remove the blocked membrane pockets mechanically. Hence, this could lead to minor membrane damages.

- **The effect of changed milieu conditions (aerobic, anaerobic) on membrane fouling**

The investigation involved a change in milieu to be realized by changing the crossflow aeration system from air to nitrogen. The cyclic milieu change, i.e. from aerobic to anaerobic and vice versa, should lead to biofilm removal or at least stopping its buildup on the membrane surface.

The permeability of the membrane module with the change in milieu declined significantly at an early stage of each setting and was recovered after intensive cleaning overnight with NaOCl (1,000 ppm) and citric acid (2 %).

The results showed that during the tests with a change in milieu conditions (aerobic, anaerobic) the biofilm layer that had built up on the membrane surface or membrane fouling due to pore blockage probably as a result of biopolymers retention were not removed.

- **The impact of membrane backwash, using a salt brine solution, on membrane performance**

The backwash with a salt brine solution between 1 % and 3 % was investigated in order to provide information on the effect of cleaning clogged membrane pores. Following the principle that a salt solution holds free charge carriers that shield the monomer charge weakening electrical interaction, the change in electrolyte concentrations was meant to remobilize ionogenic macromolecules that clog the membrane pores, allowing the blocked pores to be rinsed free.

The results showed that the brine solution had no positive impact on membrane performance. During the initial stage of experiments after the use of 1 % brine solution, an increase in permeability was observed, however the concentration of colloidal matter in the supernatant changed at the same time. Additionally, the use of higher concentrations of brine solution (2 % and 3 %) showed no positive results.

- **The impact of chemical cleaning on membrane performance**

Membrane cleaning is an integral part in the operation of ultrafiltration systems in MBRs and has a significant impact on process operations. The objective of chemical cleaning is to remove irreversible fouling that accumulates during filtration and thus prevent a sharp decline in membrane performance. Maintenance cleanings were performed approximately weekly using sodium hypochlorite. The maintenance chemical cleaning was carried out directly in the permeate tanks, to which chemicals were added.

It can be seen that preventive maintenance cleaning did not cause any significant increase in permeability. Despite chemical cleaning, the permeability even declined. This could be due to cake layer formation rather than a consequence of pore blockage. Mass transfer barriers within the fouling layer are likely to be the rate-limiting factor for chemical maintenance cleaning.

Furthermore, it was shown that the performance of intensive cleanings using sodium hypochlorite (1,000÷1,500 ppm) and citric acids (2 %) over minimum 24 hours contributed to the jump in permeability from about 40 L/(m²·h·bar) to values over 600 L/(m²·h·bar) at the MBR pilot plant (B).

- **The effect of long-term relaxation breaks on membrane performance**

Relaxation intervals are applied by shutting down the permeate flow. They are used to control the cake layer formation of membranes and to extend the intervals between maintenance cleanings. During the relaxation mode, the membranes return to their original relaxed state, as membranes are basically elastic in nature. During relaxation, the aeration of the membrane stayed in operating mode in order to assist the renewal of biomass solids in the vicinity of the membrane surface. The results showed that the permeability was recovered in these days. This means that extended relaxation intervals could alleviate membrane fouling and thus seemed to positively affect membrane performance. However, relaxation breaks involve high specific costs due to operation interruptions, i.e. low membrane throughput, that directly translates to larger membrane area.

- **Optimization of the crossflow aeration system with regard to the energy demand**

Clean water tests on oxygen transfer were performed with the fine-bubble and coarse-bubble crosslow aeration system at different air volume rates (20 m^3/h, 40 m^3/h, 60 m^3/h, and 80 m^3/h) for the optimization of the crossflow aeration system with regard to the energy demand. The specific aeration demand per membrane area SAD_m was between 0.21 and 0.62 $m^3_N/(m^2_A \cdot h)$.

The oxygen transfer rate is independent of the specific air flow rate in the investigated range. The fine-bubble crossflow aeration system could enter 20.1 g $O_2/(m^3 \cdot m)$ into clean water at a specific air flow rate of 13.22 $m^3/(m^3_{tank} \cdot h)$ or 0.4 $m^3/(m^2_A \cdot h)$. In contrast, the coarse-bubble crossflow system only achieved oxygen transfer rates of 9.9 g $O_2/(m^3 \cdot m)$ at a specific air flow rate of 13.5 $m^3/(m^3_{tank} \cdot h)$ or 0.41 $m^3/(m^2_A \cdot h)$.

The specific standard oxygen transfer efficiency (SSOTE) for the fine-bubble crossflow system was in a range of 6.25 to 6.73 %/m, whereas SSOTE for coarse-bubble crossflow system was measured as low as 3.20 to 3.44 %/m. According to a modified table of standards for compressed aeration systems *Wagner (2001)* specified SSOTEs between 6 and 8 %/m (for middle to more favorable range) in clean water for area-wide fine-bubble aeration elements. These values were achieved with the existing fine-bubble crossflow system for the middle range. Hence, the high rates of the oxygen transfer efficiency

were measured as a result of intensive mixing of the tank and due to the fine distribution of air bubbles.

The assessment of the efficiency of aeration systems is made via aeration efficiency SAE (kg O_2/kWh). According to the above-mentioned table of standards (*Wagner, 2001*), oxygen transfer efficiency rates were found to be between 3.4 and 4.5 kg O_2/kWh. The SAE values (between 4.16 and 4.47 kg O_2/kWh) that were measured for the fine-bubble crossflow system, matched the modified table of standards. In contrast, the results for the coarse-bubble crossflow system showed - as expected - lower SAEs that are in a range of 2.12 and 2.29 kg O_2/kWh. Thus, the energy consumption of the coarse-bubble crossflow system for fouling control is about two times higher than the fine-bubble crossflow system for oxygen supply.

9. Further research work

Further studies are recommended on the following topics:

- Impact of colloidal matter on membrane fouling

The investigation into the impact of the operationally defined "truly soluble fraction" < 0.04 μm on the membrane performance showed that this fraction affected membrane fouling only to a minor degree. However, it was the colloidal fraction, viz. polysaccharides and proteins, that predominantly caused the decline in permeability.

In order to investigate in detail, which colloids and/or polymeric organic matter in the fraction range between 0.45-0.04 μm are responsible for membrane fouling, further tests in series with membranes of different pore size should be carried out. After fractionating activated sludge by using different membranes (e.g. 0.2 μm, 0.1 μm, 0.04 μm), foulants, i.e. polysaccharides and proteins, should be analyzed.

- Mechanical cleaning by granulate

Mechanical cleaning by using granulate showed an overall positive effect on membrane permeability. However, further tests regarding membrane damage and resulting system failures during operation should be investigated in long-term studies.

Moreover, long-term investigations with granulate at high MLSS contents (> 15 g/L) should be carried out, as liquids with higher viscosity might protect membranes against collisions at high granulate velocities as they will then be slower.

In addition, there are questions regarding the possible impact of granulate on the biocenosis of activated sludge. After more than 600 days of operation with granulate it could not be established whether the collision frequencies of microbial aggregates and the granular material can reduce size of activated sludge flocs, leading to permeability decrease.

Currently, MBRs are mainly operated at high SRTs > 25 days. It is of great interest to know whether the application of granulate would maintain a trouble-free operation without permeability decline and the need of chemical cleaning, also for substantially shorter SRTs. The results of short-term investigations with SRTs < 15 days do not allow definite interpretation. It was observed that due to the change of SRT, sludge characteristics in the plant changed, in terms of decreasing filterability, an increase in the CST, and foaming. Therefore, investigations on potential sludge deflocculation as a result of inner repulsive force or shear force caused by granulate at low SRT are needed.

Furthermore, research on the fouling reduction via granulate should be repeated for real wastewater, in order to assess the impact of granular material on membrane surfaces, as no SEM images were taken for this membrane.

- Impact of sludge characteristics and operating conditions on membrane fouling

Despite the extensive investigation into the impact of SRT on membrane fouling, further research is needed. In particular, it is important to pay attention to temperature constancy in order to exclude temperature effects.

In the frame of this thesis it was not possible to determine, whether the sharp decline in permeability resulted from the decreasing SRT, low temperature or possibly due to the occurrence of high concentrations of colloidal matter.

- Investigation of membrane material

Research on the effect of chemical agents on membrane material could provide additional insights into the membrane condition after long-term operation, as according to *Fane (1997)* chemical agents can also attack the membrane during cleaning processes causing swelling of the membrane. After long-term membrane cleaning with chemicals, membrane should be tested using e.g. Fourier transform infrared (FTIR) spectroscopy in order to control the quality of the membrane material. This method is especially useful in measuring the degree of polymer degradation.

- Potential for crossflow optimization

The investigation into the optimization of crossflow aeration systems with regard to membrane performance should be continued. It is suggested to operate two crossflow systems, i.e. fine and coarse-bubble, in parallel under the same real conditions with activated sludge for direct comparison.

10. Summary

In this thesis, innovative and sustainable cleaning strategies were explored in order to minimize the negative environmental impact that results from the use of chemical agents and to prolong the membrane lifetime, thus reducing operating costs.

The research on permeability loss in membrane bioreactors (MBRs) and fouling reduction was carried out at three MBR pilot plants with synthetic and real wastewater. The following conclusions were drawn:

10.1. Research on permeability loss

- Influence of sludge characteristics and operating conditions on membrane fouling
  - It was shown that the concentration of the colloidal fraction obviously depends on the operating temperature and SRT. There is some evidence that this fraction contributes to fouling.
  - A nearly linear correlation was found between the colloidal fraction ($COD_{colloidal}$) and the concentration of biopolymers (proteins and polysaccharides). However, while a relationship between the retention of biopolymers and CST of activated sludge was found, a clear connection with the permeability of the investigated membranes did not exist. Further research is needed.
  - An influence of SRT on membrane fouling could not be verified due to other interrelated factors, i.e. particularly the fluctuations of temperature and wastewater compositions.
  - It was observed that adding polyaluminum chloride coagulant resulted in the reduction of the colloidal fraction of the supernatant by up to 80 % of the initial value. The coagulant even bound soluble matter $< 0.04\ \mu m$, as the COD concentration of the permeate was slightly higher.
  - Fractionation tests showed that the biological degradation of organic matter was much better during periods of low fouling and only 41 % of organic compounds were retained by the membrane in the reactor compared to 84 % during periods of high fouling. Moreover, this implies that most of the biopolymers (proteins, polysaccharides) were retained in the reactor by membrane separation.
  - The “truly dissolved constituents” from synthetic wastewater and/or activated sludge $< 0.04\ \mu m$ did not cause fouling of the membrane operated in sequence.
  - The LC-OCD analyses confirm that most of the biopolymers were rejected by the upstream membranes with nominal pore size of $0.04\ \mu m$ and thereby probably caused a decline in the permeability of these lines. Thus, by definition these biopolymers are not considered as “truly dissolved”.
  - The reason for the permeability decline of the membrane operated in sequence at enhanced flux rates up to 40 $L/(m^2 \cdot h)$ may either be the flux rate increase or the effluent composition of the upstream line.

- The rheological measurements showed a structural viscous behavior of the investigated activated sludge samples.
- It was found that with increasing MLSS concentration, the viscosity also tends to increase. The viscosity amounts to 18 mPa·s at a "common" MLSS concentration of 12 g/L in MBRs and a shear rate of 40 s^{-1}.
- A correlation between the apparent viscosity and the retention of proteins and polysaccharides in the supernatant of activated sludge was observed.
- The coefficients of both model approaches (Oswald de Waele and Herschel-Bulkley) could be described as a function of MLSS concentration using a non-linear regression analysis. However, the Oswald de Waele approach showed a better plausibility with the measures values.

10.2. Research on fouling reduction

- Application of mechanical cleaning with granular material in MBR
  - It was found out that the use of granular material:
    - causes a positive effect on membrane permeability (long-term membrane operation without permeability decrease at high flux rates up to 35 L/(m^2·h))
    - provides a high flux enhancement (> 27 %)
    - does not negatively affect the effluent quality
    - meets the membrane's functional requirements of biomass separation
  - SEM images and integrity tests showed that in consequence of abrasive cleaning the granular material leaves brush marks on the membrane surface, but all the same the membrane function is not affected.
  - Membrane operation at high flux rates (> 35 L/(m^2·h)) causes a significant decline in permeability, presumably as a result of permeation drag forces that might draw the particulate and colloidal matter towards the membrane surface.
  - The use of granular material has an overall positive effect on membrane operation, as less cleaning is necessary and higher flux rates are realizable, and still the effluent quality stays the same. Granulate does not show any negative impact on the membrane function, which is to separate activated sludge and treated wastewater.
  - It was demonstrated that the findings from MBR pilot plant operation with synthetic wastewater could also be applied to real conditions.
- Effect of changed milieu conditions (aerobic, anaerobic) on membrane fouling
  - The results showed that during the tests with a change in milieu conditions (aerobic, anaerobic) the biofilm layer that had built up on the membrane surface or membrane fouling due to pore blockage probably as a result of biopolymers retention were not removed. Instead, an even stronger decline in permeability was observed.
- Impact of membrane backwash, using a salt brine solution, on membrane performance
  - The brine solution had no positive impact on membrane performance compared with the standard backwash with permeate. In the initial stage of experiments, an increase in per-

meability was observed after the use of 1 % brine solution, however the concentration of colloidal matter in the supernatant changed at the same time. Additionally, the use of higher concentrations of brine solution (2 % and 3 %) also showed no positive results.

- Impact of chemical cleaning on membrane performance
  - Preventive maintenance cleanings, using sodium hypochlorite (200 ppm for the MBR plant A; 500÷1,000 ppm for the MBR pilot plant B) caused no significant increase in permeability. Despite chemical cleaning, the permeability even declined.
  - It was shown that the performance of intensive cleanings, using sodium hypochlorite (1,000÷1,500 ppm) and citric acids (2 %) over minimum 24 hours contributed to the jump in permeability from about 40 L/(m²·h·bar) to values over 600 L/(m²·h·bar).
- Effect of long-term relaxation breaks on membrane performance
  - Relaxation breaks proved to enhance membrane performance; however, these involve high specific costs due to operation interruptions, i.e. low membrane throughput.
- Optimization of the crossflow aeration system with regard to the energy demand
  - The specific standard oxygen transfer efficiency (SSOTE) for the fine-bubble crossflow system was in a range of 6.25 to 6.73 %/m, whereas SSOTE for coarse-bubble crossflow system was measured as low as 3.20 and 3.44 %/m. Only the high rates of SSOTE for fine-bubble crossflow system matched a modified table of standards for compressed aeration systems due to intensive mixing of the tank and the fine distribution of air bubbles
  - The oxygen transfer efficiency (SAE) rates (between 4.16 and 4.47 kg O_2/kWh) that were measured for the fine-bubble crossflow system, complied with the modified table of standards. In contrast, the results for the coarse-bubble crossflow system showed - as expected - lower SAEs that are in a range of 2.12 and 2.29 kg O_2/kWh. Thus, the energy consumption of the coarse-bubble crossflow system for fouling control is about two times higher than the fine-bubble crossflow system for oxygen supply.

REFERENCES

Adam, C., Kraume, M., Gnirss, R., Lesjean, B. (2001) Vermehrte biologische Phosphorelimination in Membranbioreaktoren. Begleitbuch zur 4. Aachener Tagung Siedlungswasserwirtschaft und Verfahrenstechnik, Aachen.

Al-Halbouni, D. (2008) Role of extracellular polymeric substances and metals in fouling of membranes in the wastewater treatment. PhD thesis, RWTH Aachen, Germany.

Al-Malack, M. H., Anderson, G. K. (1997) Use of crossflow microfiltration in wastewater treatment. Water Research 31(12), pp. 3064-3072.

Altmann, J., Ripperger, S. (1997) Particle deposition and layer formation at the crossflow microfiltration. Journal of Membrane Science 124(1), pp. 119-128.

APHA, AWWA, WEF, (1998) Standard Methods for the Examination of Water and Wastewater. American Public Health Association, American Water Works Association and Water Environment Federation, Washington DC, USA.

Arkhangelsky, E., Kuzmenko, D., Gitis, N. V., Vinogradov, M., Kuiry, S., Gitis, V. (2007) Hypochlorite Cleaning Causes Degradation of Polymer Membranes. Chemistry and Materials Science 28(2), pp. 109-116.

Arnal, J. M., GarciaFayos, B., Sancho, M., Verdu, G. (2009) Ultrafiltration membrane cleaning with different chemical solutions after treating surface water. Desalination and Water Treatment 7, pp. 198-205.

ATV–DVWK-A 131, (2000a) Arbeitsblatt zur Bemessung von einstufigen Belebungsanlagen. GFA.

ATV-DVWK, (2000b) Membranbelebungsverfahren, KA Wasserwirtschaft, Abwasser, Abfall, 47. Jahrgang, Nr. 10, S. 1547 – 1553.

ATV-DVWK, (2002) Aufbereitung von Industrieabwasser mit Membranverfahren und Membranbelebungsverfahren - Teil 1: Membranverfahren, ISBN 3-936514-15-1.

ATV-Handbuch, (1997) Biologische und weitergehende Abwasserreinigung. 4. Auflage Ernst & Sohn.

AWWA, (2005) Microfiltration and Ultrafiltratiion Membranes in Drinking Water. American Water Works Association.

Bacchin, P., Si-Hassen, D., Starov, V., Clifton, M.J., Aimar, P. (2002) A unifying model for concentration polarisation, gel-layer formation and particle deposition in cross-flow membrane filtration of colloidal suspensions. Chemical Engineering Science 57(1), pp. 77-91.

Bae, T. H., Tak, T. M. (2005) Interpretation of fouling characteristics of ultrafiltration membranes during the filtration of membrane bioreactor mixed liquor, Journal of Membrane Science 264(1-2), pp. 151–160.

Baker, R. (2000) Membrane Technology and Applications. McGraw-Hill, New York.

Baker, R. (2004) Membrane Technology and Applications. 2nd ed., Wiley.

Barker, D. J., Stuckey, D. C. (1999) A review of soluble microbial products (SMP) in wastewater treatment systems. Water Research 33(14), pp. 3063-3082.

Barker, D. J., Salvi, S. M. L., Langenhoff, A. A. M, Stuckey, D. C. (2000) Soluble microbial products in ABR treating low-strength wastewater. Environmental Engineering 126(3), pp. 239-240.

Baumgarten, S. (2007) Membranbioreaktoren zur industriellen Abwasserreinigung. Dissertation: RWTH Aachen, 03 Fakultät für Bauingenieurwesen.

Beier, S. P. (2007) Pressure driven membrane processes. ISBN 87-7681-152-2.

Belford, G., Davis, R. H., Zydney, A. L. (1994) The behavior of suspensions and macromolecular solutions in cross flow microfiltration. Journal of Membrane Science 96(1-2), pp. 1-58.

Bowen, W. R., Jenner, F. (1995) Theoretical description of membrane filtration of colloids and fine particles: an assessment and review. Advances in Colloid and Interface Science 56, pp. 141-200.

Bouhabila, E. H., Aim, R. Ben., Buisson, H. (1998) Microfiltration of activated sludge using submerged membrane with air bubbling. Desalination 118(1-3), pp. 315-322.

Bouhabila, E. H., Ben Aim, R., Buisson, H. (2001) Fouling characterisation in membrane bioreactors. Separation and Purification Technology 22-23, pp. 123-132.

Cha, G., Jeong, T., Yoo, I., Kim, D. (2004) Kinetics Characteristics of SMP and ECP in Relation of Loading Rate in a MBR process. Begleitband zur IWA Specialty Conference – Water Environment – Membrane Technology, M-2-4, Seoul, Korea.

Chang, I. S., Lee, C. H. (1998) Membrane filtration characteristics in membrane-coupled activated sludge system-the effect of physiological states of activated sludge on membrane fouling. Desalination 120(3), pp. 221-233.

Chang, I. S., Le Clech, P., Jefferson, B., Judd, S. (2002) Membrane Fouling in Membrane Bioreactors for Wastewater Treatment. Journal of Environmental Engineering 128(11), pp. 1018-1029.

Chang, I. S., Kim, S. N. (2005) Wastewater treatment using membrane filtration - effect of biosolids concentration on cake resistance. Process biochemistry 40(3-4), pp. 1307-1314.

Chellam, S., Wiesner, M. R. (1992) Particle transport in clean membrane filters in laminar flow. Environmental Science and Technology 26(8), pp. 1611-1621.

Chen, G. W., Lin, W. W., Lee, D. J. (1996) Capillary suction time (CST) as a measure of sludge dewaterability. Water Science and Technology 34(3-4), pp. 443-448.

Chen, D., Weavers, L.K., Walker, H.W. (2006) Ultrasonic control of ceramic membrane fouling by particles: effect of ultrasonic factors. Ultrasonics Sonochemistry 13(5), pp. 379-387.

Cho, B. D., Fane, A. G. (2002) Fouling transients in nominally sub-critical flux operation of a membrane bioreactors. Journal of Membrane Science 209(2), pp. 391-403.

Churchouse, S., Warren, S., Floyd, M. (2008) Feedback from the Porlock MBR Plant in its 10th Year of Operation:- An Analysis of the Flux, Effluent Quality and Membrane Lifetime Data to date. Proceedings paper by SJC October 2008 Aachen.

Cicek, N., Winnen, H., Suidan, M. T., Wrenn, B. E., Urbain, V., Manem, J. (1998) Effectiveness of the membrane bioreactor in the biodegradation of high molecular weight compounds. Water Research 32(5), pp. 1553-1563.

Cicek, N., Macomber, J., Davel, J., Suidan, M. T., Audic, J., Genestet, P. (2001) Effect of solids retention time on the performance and biological characteristics of a membrane bioreactor. Water Science and Technology 43(11), pp. 43-50.

Cicek, N. (2003a) A review of membrane bioreactors and their potential application in the treatment of agricultural wastewater. Canadian Biosystems Engineering 45, pp. 6.37-6.49.

Cicek, N., Suidan, M. T., Ginestet, P., Audic, J. M. (2003b) Impact of soluble organic compounds on permeate flux in an aerobic membrane bioreactor. Environmental Technology 24(2), pp. 249-56.

Cornel, P., Wagner, M., Krause, S. (2001) Sauerstoffeintrag in Membranbelebungsanlagen. Membrantechnik 4 – Beitrag A14 zur Aachener Tagung Siedlungswasserwirtschaft und Verfahrenstechnik.

Cornel, P., Wagner, M., Krause, S. (2002) Investigation of oxygen transfer rates in full scale membrane bioreactors, IWA annual conference, Melbourne, Australia. Paper reference no. e21291a.

Côté, P., Buisson, H., Praderie, M. (1998) Immersed membranes activated sludge process applied to the treatment of municipal wastewater. Water Science and Technlogy 38(4-5), pp. 437-442.

Cui, Z. F., Chang, S., Fane, A. G. (2003) The Use of Gas Bubbling to Enhance Membrane Processes. Journal of Membrane Science 221(1-2), pp. 1-35.

De Boer, R., Zomerman, J. J., Hiddink, J., Aufderheyde, J., van Swaay, W. P. M., Smolders, C. A. (1980) Fluidized beds as turbulence promoters in the concentration of food liquids by reverse osmosis. Journal of Food Science 45(6), pp. 1522-1528.

Defrance, L., Jaffrin, M. Y., Gupta, B., Paullier, P., Geaugey, V. (2000) Contribution of various constituents of activated sludge to membrane bioreactor fouling. Bioresource Technology 73(2), pp. 105-112.

DIN 38408, part 23. (1987) Gasförmige Bestandteile (Gruppe G); Bestimmung des Sauerstoffsättigungsindex.

DIN 38409, part 2. (1987) Gravimetrische Bestimmung der mittels Papierfilter abfiltrierbaren Stoffe.

Dorgeloh, E. (2004) Leistungsfähigkeit, insbesondere Nährstoffelimination, des Membranbelebungsverfahrens. ATV-DVWK Membrantagung, Tagungsband, Kassel.

Drews, A., Kraume, M. (2005) Process Improvement by Application of Membrane Bioreactors. Chemical Engineering Research and Design 83(3), pp. 276-284.

Drews, A., Mante, J., Iversen, V., Vocks, M., Lesjean, B., Kraume, M. (2007) Impact of ambient conditions on SMP elimination and rejection in MBRs. Water Research 41(17), pp. 3850-3858.

Drews, A., Vocks, M., Bracklow, U., Iversen, V., Kraume, M. (2008) Does fouling in MBRs depend on SMP? Desalination 231(1-3), pp. 141-149.

Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., Smith, F. S. (1956) Colorimetric method for determination of sugars and related substances. Analytical Chemistry 28(3), pp. 350-356.

DWA, (2007) Treatment of industrial wastewater and process water with membrane processes and membrane bioreactor. DWA-Topics, ISBN 978-3-940173-55-3.

DWA, (2007b) Messung der Sauerstoffzufuhr von Belüftungseinrichtungen in Belebungsanlagen in Reinwasser und in belebtem Schlamm. Merkblatt M 209, Gesellschaft zur Förderung der Abwassertechnik e.V. (GFA), Hennef.

Engelhardt, N., Firk, W. (2000) Erste Betriebserfahrungen mit dem Membranbelebungsverfahren auf der kommunalen Kläranlage Rödingen (3.000 EW). Begleitbuch zur 3. Aachener Tagung Siedlungswasserwirtschaft und Verfahrenstechnik, Aachen.

Engelhardt, N. (2003) Membranbelebungsverfahren – eine beherrschbare und erfolgreiche Technik – Erfahrungen nach vierjährigem Betrieb. Beitrag A 1 zur 5. Aachener Tagung Siedlungswasserwirtschaft und Verfahrenstechnik, Membrantechnik 5, Aachen.

Evenblij, H. (2006) Filtration Characteristics in Membrane Bioreactors. PhD thesis, Delft Technical University, The Netherlands.

Fan, L., Harris, J. L., Roddick, F. A., Booker, N. A. (2001) Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. Water Research 35(18), pp. 4455-4463.

Fan, F., Zhou, H., Husain, H. (2006) Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor processes. Water Research 40(2), pp. 205-212.

Fane, A. G. (1996) Membranes for water production and wastewater reuse. Desalination 106(1-3), pp. 1–9.

Fane, A. G. (1997) Control of concentration polarisation in membrane process by process operation strategies and module design. Proceedings of the Symposium on Characterization of Polymers with Surface, Lappeenranta, Finland.

Fane, A. G., Fane, S. A. (2005a) The role of membrane technology in sustainable decentralized wastewater systems. Water Science and Technology 15(10), pp. 317-325.

Fane, A.G. (2005b) Towards sustainability in membrane processes for water and wastewater processing, in: Proceedings of the International Congress on Membranes and Membrane Processes (ICOM), Seoul, Korea.

Fang, H., Shi, X., Zhang, T. (2006) Effect of activated carbon on fouling of activated sludge filtration. Desalination 189(1-3), pp. 193-199.

Fick, A. (1855) Über Diffusion. Annalen der Physik 170(1), pp. 59-86.

Field, R. W., Howell, Wu. D., Gupta, B. B. (1995) Criticl flux concept for microfiltration fouling. Journal of Membrane Science 100(3), pp. 259-272.

Frolund, B., Palmgren, R., Keiding, K., Nielsen, P. H. (1996) Extraction of extracellular polymers from activated sludge using a cation exchange resin. Water Research 30(8), pp. 1749-1758.

Gander, M. A., Jefferson, B., Judd, S. J. (2000) Membrane bioreactors for use in small wastewater treatment plants: membrane materials and effluent qualities. Water Science and Technology 41(1), pp. 205-211.

Germain, E., Stephenson, T., Pearce, P. (2005) Biomass Characteristics and Membrane Aeration: Toward a Better Understanding of Membrane Fouling in Submerged Membrane Bioreactors (MBRs). Wiley InterScience.

Gnirss, R., Lesjean, B., Adam, C., Buisson, H. (2003) Cost effective and advanced phosphorus removal in membrane bioreactors for a decentralised wastewater technology. Water Science and Technology 47(12), pp. 133–139.

Gorenflo, A. (2003) Rückhalt und Fouling von natürlichen organischen Stoffen bei der Nano- und Ultrafiltration, PhD thesis, University of Karlsruhe, Germany.

Grelier, P., Rosenberger, S., Tazi-Paina, A. (2006) Influence of sludge retention time on membrane bioreactor hydraulic performance. Desalination 192(1-3), 10-17.

Grélot, A., Busnot, A., Grelier, P., Tazi-Pain, A., Heijnen, M., Grasmick, A. (2009) A new and appropriate fibre sheet configuration for MBR technologies. Desalination and Water Treatment 6, pp. 25-32.

Guglielmi, G., Chiarani, D., Saroj, D. P., Andreottola, G. (2008) Impact of chemical cleaning and air-sparging on the critical and sustainable flux in a flat sheet membrane bioreactor for municipal wastewater treatment. Water Science and Technology 57(12), pp. 1873-1879.

Gui, P., Huang, X., Chen, Y., Qian, Y. (2003) Effect of operational parameters on sludge accumulation on membrane surfaces in a submerged membrane bioreactor. Desalination 151(2), pp. 185-194.

Günder, B. (1999) Das Membranbelebungsverfahren in der kommunalen Abwasserreinigung. Stuttgarter Berichte zur Siedlungswasserwirtschaft; Bd.153.

Haberkamp, J., Ruhl, A. S., Ernst, M., Jekel, M. (2007) Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behaviour in ultrafiltration. Water Research 41, pp. 3794–3802.

Henkel, J., Lemac, M., Wagner, M., Cornel, P. (2009) Oxygen transfer in membrane bioreactors treating synthetic greywater. Water Research 43(6), pp. 1711-1719.

Henkel, J., Cornel, P., Wagner, M. (2009) Free water content and sludge retention time: impact on oxygen transfer in activated sludge. Environmental Science and Technology 43(22), pp. 8561-8565.

Henze, M,. Gujer, W., Mino, T., Wentzel, M. C., Marais, G. v. R., Van Loosdrecht, M. C. M. (1999) Activated Sludge Model No. 2d. Activated Sludge Models ASM 1, ASM2, ASM2D and ASM3 edited by IAW Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment Scientific and Technical Report No 9, IWA Publishing, London, 2000, pp. 75-98.

Hong, S. P, Bae, T. H., Tak, T. M., Hong, S., Randall, A. (2002) Fouling control in activated sludge submerged hollow fiber membrane bioreactors. Desalination 143(3), pp. 219-228.

Howe, K. J., Clark, M. M. (2002) Fouling of microfiltration and ultrafiltration membranes by natural waters. Environmental Science and Technology 36(16), pp. 3571-3576.

Huang, X., Liu, R., Qian, Y. (2000) Behaviour of soluble microbial products in a membrane bioreactor. Process Biochemistry 36(5), pp. 401-406.

Itonaga, T., Kimura, K., Watanabe, Y. (2004) Influence of suspension viscosity and colloidal particles on permeability of membrane used in membrane bioreactor (MBR). Water Science and Technology 50(12), pp. 301-309.

Iversen, V., Bonnet, L., Drews, A., Lesjean, B, Kraume, M. (2006) Can we control the fouling with flux enhancing chemicals? EUROMBRA Workshop, Trondheim.

Jacangelo, J. G. (1997) Membrane Filtration for Microbial Removal, American Water Works Association.

Jarusutthirak, C., Amy, G. (2001) Membrane filtration of wastewater effluents for reuse: effluents organic matter rejection and fouling. Water Science and Technology 43(10), pp. 225-232.

Jefferson, B., Laine, A. L., Judd, S. J., Stephenson, T. (2000) Membrane bioreactors and their role in wastewater reuse. Water Science and Technology 41(1), pp. 197-204.

Jiang, T., Kennedy, M. D., Guinzbourg, B. F., Vanrolleghem, P. A., Schippers, J. C. (2005) Optimising the operation of a MBR pilot plant by quantitative analysis of the membrane fouling mechanism. Water Science and Technology 51(6-7), pp. 19-25.

Jiang, T. (2007) Characterization and Modelling of Soluble Microbial Products in Membrane Bioreactors. PhD thesis, Ghent University, Belgium.

Jin, B., Wilén, B. M., Lant, P. (2004) Impacts of morphological, physical and chemical properties of sludge flocs on dewaterability of activated sludge. Chemical Engineering 98(1-2), pp. 115-126.

Jönsson, A.S. (1995) Concentration polarisation and fouling during ultrafiltration of colloidal suspensions and hydrophobic solutes. Separation Science and Technology 30(2), pp. 301-312.

Judd, S. (2004) A review of fouling of membrane bioreactors in sewage treatment. Water Science and Technology 49(2), pp. 229-235.

Judd, S. (2006) The MBR Book: Principles and Applications of Membrane Bioreactors in Water and Wastewater Treatment. Elsevier, Oxford.

Khan, S. J. (2008) Influence of hydrodynamic and phisico-chemical approaches on fouling mitigation in a membrane bioreactor. PhD Thailand.

Kim, J. S., Lee, C. H., Chang, I. S. (2001) Effect of pump shear on the performance of a crossflow membrane bioreactor. Water Research 35(9), pp. 2137-2144.

Kim, J. S. and Lee, C. H. (2003) Effect of powdered activated carbon on the performance of n aerobic membrane bioreactor: comparison between cross-flow and submerged membrane systems. Water Environment Research 75(4), pp. 300-307.

Klegraf, F. (2006) Beherrschung von Fouling und Scaling an getauchten Filtrationssystemsn in Membranbelebungsanlagen. Membrantechnik in der Abwasserwirtschaft. Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V. (DWA).

Kraume, M., Bracklow, U., Drews, A., Vocks, M. (2005) Process configurations for biotreatment: MBR concepts for biological nutrients removal. Presented at the School of Water Sciences, 1 day conference on January 28th 2005, © 2005 Cranfield University.

Krause, S. (2005) Untersuchungen zum Energiebedarf von Membranbelebungsanlagen, Schriftenreihe WAR, Band 166, Dissertation.

Kubin, K. (2004) Einfluss unterschiedlicher Verfahrenskonzepte auf Substratabbau und Nährstoffverwertung in Membran-belebungsanlagen zur kommunalen Abwasserreinigung. Dissertationsschrift vorgelegt an der Fakultät III – Prozesswissenschaften der Technischen Universität Berlin.

Laspidou, Ch. S., Rittmann, B. E. (2002) A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass. Water Research 36(11), pp. 2711-2720.

Le Clech, P., Jefferson, B., Chang, I. S., Judd, S. (2003) Critical flux determination by the flux-step method in a submerged membrane bioreactor. Journal of Membrane Science 227(1-2), pp. 81-93.

Lee, J., Ahn, W. Y., Lee, C. H. (2001) Comparison of the filtration characteristics between attached and suspended growth microorganisms in submerged membrane bioreactor. Water Research 35(10), pp. 2435-2445.

Lee, Y., Cho, J., Seo, Y, Lee, J. W., Ahn, K.-H. (2002) Modeling of submerged membrane bioreactor process for wastewater treatment. Desalination 146(1-3), 451-457.

Lemmer, H. (1990) Die mikroskopische Untersuchung von belebtem Schlamm und ihre Bewertung. Münchner Beiträge zur Abwasser-, Fischerei- und Flußbiologie Band 45, 176-191.

Lesjean, B., Gnirss, R., Adam, C., Kraume, M., Luck, F. (2003) Enhanced biological phosphorus removal process implemented in membrane bioreactors to improve phosphorous recovery and recycling. Water Science and Technology 48(1), pp. 87–94.

Li, Y. Z., He, Y. L., Liu, Y. H., Yang, S. C., Zhang, G. J. (2005) Comparison of the filtration characteristics between biological powdered activated carbon sludge and activatedsludge in submerged membrane bioreactors. Desalination 174(3), pp. 305–314.

Lim, A. L., Renbi Bai. (2003) Membrane fouling and cleaning in microfiltration of activated sludge wastewater. Journal of Membrane Science 216(1-2), pp. 279-290.

Lorain, O, Dufaye, P. E., Bosq, W., Espenan, J. M. (2010) A new membrane bioreactor generation for wastewater treatment application: Strategy of membrane aeration management by sequencing aeration cycles. Desalination 250(2), pp. 639-643.

Lotito, V., Spinosa, L., Mininni, G., Antonacci, R. (1997) The Rheology of Sewage Sludge at Different Steps of Treatment. Water Science and Technology 36(11), pp. 79-85.

Lowe, E., Durkee, E. L. (1971) Dynamic turbulence promotion in reverse osmosis processing of liquid foods. Journal of Food Science 36(1), pp. 31-32.

Lowry, O. H., Rosebrough, N. J., Farr, A. L., Randall, R. J. (1951) Protein measurement with the folin phenol reagent. Journal of Biological Chemistry 193, pp. 265-275.

Lu, S. G., Imai, T., Ukita, M., Sekine, M., Higuchi, T., Fukagawa, M. (2001) A model for membrane bioreactor process based on the concept of formation and degradation of soluble microbial products. Water Research 35(8), pp. 2038-2048.

Madaeni, S. S., Fane, A. G., Wiley, D. E. (1999) Factors influencing critical flux in membrane filtration of activated sludge. Journal of Chemical Technology and Biotechnology 74 (6), pp. 539-543.

Malamis, S., Andreadakis, A. (2009) Fractionation of proteins and carbohydrates of extracellular polymeric substances in a membrane bioreactor system. Bioresource Technology 100(13), pp. 3350-3357.

Massé, A., Sperandio, M., Cabassud, C. (2006) Comparison of sludge characteristics and performance of a submerged membrane bioreactor and an activated sludge process at high solids retention time. Water Research 40(12), pp. 2405-2415.

Melin, T., Jefferson, B., Bixio, D., Thoeye, C., De Wilde, W., De Koning, J., Van der Graaf, J., Wintgens, T. (2006) Membrane bioreactor technology for wastewater treatment and reuse. Desalination 187(1-3), pp. 271-282.

Melin, T., Rautenbach, R. (2007) Membranverfahren: Grundlagen der Modul- und Anlagenauslegung. Springer-Verlag, Berlin. 3., aktualisierte und erweiterte Auflage.

Meng, F., Zhang, H., Li, Y., Xiao, J., Zhang, X. (2006) Effect of filamentous bacteria on membrane fouling in submerged membrane bioreactor. Journal of Membrane Science 272(1-2), pp. 161-168.

Michaels, A. S. (1968) New separation technique for the CPI. Chemical Engineering Progress 64(12), pp. 31 – 43.

MUFV, (2007) Steigerung der Energieeffizienz von Abwasseranlagen. Ministerium für Umwelt, Forsten und Verbraucherschutz Rheinland Pfalz.

Mulder, M. (2000) Basic Principles of Membrane Technology. Kluwer Academic Publishers, Dordrecht.

Nagaoka, H., Ueda, S., Miya, A. (1996) Influence of bacterial extracellular polymers on the membrane separation activatd sludge process. Water Science and Technology 34(9), pp. 165-172.

Ng, C. A., Sun, D., Fane, A. (2006) Operation of membrane bioreactor with powdered active carbon addition. Separation Science and Technology 418), pp. 1447-1466.

Noordman, T. M. (2000) High Flux Ultrafiltration. PhD thesis, Groningen University, the Netherlands.

Pan, J. R., Su, Y. Ch., Huang, Ch. (2010) Characteristics of soluble microbial products in membrane bioreactor and its effect on membrane fouling. Desalination 250(2), pp. 778-780.

Pan, J. R., Su, Y. Ch., Huang, Ch., Lee, H. Ch. (2010) Effect of sludge characteristics on membrane fouling in membrane bioreactors. Journal of Membrane Science 349(1-2), pp. 287-294.

Panglisch, S., Holy, A., Urban, F., Dautzenberg, W., Sous, P., Ohligschläger, J., Gimbel, R. (2005) Transferring pilot experiments into the planning of Germany's largest two-stage ultrafiltration plant. Desalination 179(1-3), pp. 225-235.

Peinemann, K. V., Pereira Nunes, S. (2010) Membrane Technology: Volume 4: Membranes for Water Treatment. Wiley VCH Verlag GmbH.

Pinnekamp, J., Baumgarten, S., Charwath, C., Schröder, H. Fr., Lange, M. (2006) Machbarkeitsuntersuchungen zum Einsatz einer Membranbelebungsanlage am Kläranlagenstandort Wuppertal Buchenhofen; Abschlussbericht zum gleichnamigen Forschungsvorhaben im Auftrag des MUNLV-NRW.

Poele, s. T., van der Graff, J. (2005) Enzymatic cleaning in ultrfiltration of wastewater treatment plant effluent. Desalination 179(1-3), pp. 73-81.

Pollice, A., Laera, G., Saturno, D., Giordano, C. (2008) Effects of sludge retention time on the performance of a membrane bioreactor treating municipal sewage. Journal of Membrane Science 317(1-2), pp. 65-70.

Rautenbach, R. (1997) Membranverfahren: Grundlagen der Modul- und Anlagenauslegung. Springer-Verlag, Berlin.

Reicherter, E. (2003) Untersuchungen zur Kennzahlen als Grundlage für Kostenbetrachtungen in der Abwasserentsorgung; Universität der Bundeswehr München, Inst. für Wasserwesen, Mitteilungen Heft 84, Kommissionsverlag Oldenburg Industrieverlag GmbH, München.

Rios, G. M., Rakatotoarisoa, H., Tarodo de la Fuente, B. (1987) Basic transport mechanics of ultrafiltration in the presence of fluidized particles. Journal of Membrane Science 34(3), pp. 331-343.

Ripperger, S. (1992) Mikrofiltration mit Membranen: Grundlagen, Verfahren, Anwendungen. VCH-Verlagsgesellschaft, Weinheim.

Roorda, J. H. (2004) Filtration characteristics in dead-end ultrafiltration of wwtp-effluent. Ph.D. Dissertation, Delft University of Technology, Delft.

Rosenberger, S., Schreiner, A., Wiesmann, U., Kraume, M. (2001) Impact of different sludge ages on the performance of membrane bioreactors. Proceedings IWA Berlin World Water Congress.

Rosenberger, S., Kruger, U., Witzig, R., Manz, W., Szewzyk, U., Kraume, M. (2002) Performance of a bioreactor with submerged membranes for aerobic treatment of municipal waste water. Water Research 36(2), pp. 413-420.

Rosenberger, S. (2003) Charakterisierung von belebtem Schlamm in Membranbelebungsreaktoren zur Abwasserreinigung. VDI Reihe 3, Nr. 769, Dissertation.

Rosenberger, S., Evenblij, H., te Poele, S., Wintgens, T., Laabs, C. (2005) The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes—six case studies of different European research groups. Journal of Membrane Science 263(1-2), pp. 113-126.

Rosenberger, S., Laabs C., Lesjean B., Gnirss R., Amy G., Jekel M., Schrotter J.-C. (2006) Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment. Water Research 40(4), 710-720.

Schier, W. (2003) Ein exemplarischer Ansatz zur Einbindung neuer Bemessungswege und neuer Reinigungstechnologien bei der Ertüchtigung von Kläranlagen. Kassel: Kassel Univ. Press. Schriftreihe des Fachgebietes Siedlungswasserwirtschaft, Wasser-Abwasser-Umwelt, Bd. 22, Dissertation.

Schier, W., Frechen, F. B., Fischer, St. (2009) Efficiency of mechanical pre-treatment on European MBR plants. Desalination 236(1-3), pp. 85-93.

Schiener, P., Nachaiyasit, S., Stuckey, D. C. (1998) Production of soluble microbial products (SMP) in an anaerobic baffled reactor. Environmental technology 19(4), pp. 391-399.

Sen Gupta, B., Hasan, S., Hashim, M. A., Cui, Z. F. (2005) Effects of colloidal fouling and gas sparging on microfiltration of yeast suspension. Bioprocess and Biosystems Engineering 27(6), pp. 407-413.

Slatter, P., T. (1997) The Rheological Characterization of Sludges. Waater Science and Technology 36(11), pp. 9-18.

Sombatsompop, K. (2007) Membrane Fouling Studies in Suspended and Attached Growth Membrane Bioreactor Systems. PhD thesis, Asian Institute of Technology, Thailand.

Staude, E. (1992) Membranen und Membranprozesse. VCH- Verlagsgesellschaft, Weinheim.

Stein, S., Walter, H., Zastrow, P. (2001) Kläranlage Markranstädt – Betriebsergebnisse einer Membranbelebungsanlage für 12.000 EW. Begleitbuch zur 4. Aachener Tagung Siedlungswasserwirtschaft und Verfahrenstechnik, Aachen.

Stein, S. (2003) Erfahrungen im Betrieb mit unterschiedlichen Membransystemen. Tagungsunterlagen der ATV-DVWK Membrantage, Bonn.

Stephenson, T., Brindle, K., Judd, S., Jefferson, B. (2000) Membrane Bioreactors for Wastewater Treatment. IWA Publishing, London.

Tang, C. Y., Fu, Q. S., Criddle, C. S., Leckie, J. O. (2007) Effect of flux (transmembrane pressure) and membrane properties on fouling and rejection of reverse osmosis and nanofiltration membranes treating perfluorooctane sulfonate containing wastewater. Environmental Science and Technology 41(6), pp. 2008-2014.

Thiruvenkatachri, R., Shim, W. G., Lee, J. W., Moon, H. (2004) Effect of powdered activated carbon type on the performance of an adsorption-microfiltration submerged hollow fiber membrane hybrid system. Korean Journal of Chemical Engineering 21(5), pp. 1044-1052. Springer New York.

Trussell, R., Adham, S., Tchobanoglous, G. (2003) Testing protocols for membrane selection: equivalency and fate, organism/pathogen removal. Proceedings IDA Conference on Water Reuse and Desalination, Singapore.

Trussell, R. S., Merlo, R. P., Hermanowicz, S. W., Jenkins, D. (2007) Influence of mixed liquor properties and aeration intensity on membrane fouling in a submerged membrane bioreactor at high mixed liquor suspended solids concentrations. Water Research 41(5), pp. 947-958.

Ueda, T., Hata, K, Kikuoka, Y., Seino, O. (1997) Effects of aeration on suction pressure in a submerged membrane bioreactor. Water Research 31(3), pp. 489-494.

USEPA, (2005) Membrane Filtration Guidance Manual. EPA 815-R-06-009. Office of Water, Washington, D.C.

Van der Velden, P. M. (1976) New membranes for hyperfiltration processes. Synthesis, properties and applications. PhD thesis University of Twente, Enschede, the Netherlands.

Van der Waal, M. J., van der Velden, P. M., Koning, J., Smolders, C. A. van Swaay, W. P. M. (1977) Use of Fluidized Beds as turbulence Promoters in Tubular Membrane Systems. Desalination 22(1-3), pp. 465-483.

Verrecht, B., Judd, J., Guglielmi, G., Brepols, C., Mulder, J. W. (2008) An aeration energy model for an immersed membrane bioreactor. Water Research 42, pp. 4761-4770.

Vigneswaran, S., Guo, W. S., Smith, P., Ngo, H. H. (2007) Submerged membrane adsorption hybrid system (SMAHS): Process control and optimization of operating parameters. Desalination 202(1-3), pp. 392-399.

Visvanathan, C., Bein Aim, R., Parameshwaran, K. (2000) Membrane Separation Bioreactors for Wastewater Treatment. Critical Reviews in Environmental Science and Technology 30(1), pp. 1-48.

Vocks, M., Adam, C., Lesjean, B., Gnirss, R., Kraume, M. (2005) Enhanced post-denitrification without addition of an external carbon source in membrane bioreactors. Water Research 39(14), pp. 3360-3368.

Yoon, S. H., Kim, H. S., Yeom, I. T. (2004) Optimization model of submerged hollow fiber membrane modules. Journal of Membrane Science 234(1-2), pp. 147-156.

Yoon, S. H., Collins, J. H. (2006) A novel flux enhancing method for membrane bioreactor (MBR) process using polymer. Desalination 191(1-3), pp. 52-61.

Yuan, W., Zydney, A. L. (2000) Humic Acid Fouling during Ultrafiltration. Environmental Science and Technology 34(23), pp. 5043-5050.

Wagner, M. (2001) Entwicklungstendenzen bei Belüftungssystemen – eine Übersicht, Begleitband zur 2. Hannoversche Belüftertagung, Hannover, 17.

Wang, Z., Wu, Z., Yu, G., Liu, J., Zhou, Z. (2006) Relationship between sludge characteristics and membrane flux determination in submerged membrane bioreactors. Journal of Membrane Science 284(1-2), pp. 87-94.

Wang, X., Wu, Z., Wang, Z., Du, X., Hua, J. (2008) Membrane fouling mechanisms in the process of using flat-sheet membrane for simultaneous thickening and digestion of activated sludge. Separation and Purification Technology 63(3), pp. 676-683.

Wasp, E. J., Kenny, J. P., Gandhi, J. N. (1977) Solid Liquid Flow in Slurry pipeline transportation. 1st Edition, Trans Tech Publications.

Wedi, D. (2005) Energiebedarf und Wirtschaftlichkeit des Membranbelebungsverfahren. In Proceedings of the conference of DWA and DVGW, 21- 23.06, Osnabrück.

Wedi, D., Joss, A. (2008) Dimensioning of membrane bioreactors for municipal wastewater treatment. Water Science and Technology 57(6), pp. 829-835.

Wenten, I. G. (2002) Recent development in membrane science and its industrial applications. Songklanakarin Journal of Science and Technology 24 (Suppl.), pp. 1009-1024.

Wett, M. (2005) Foulingverhalten des Membranbelebungs-verfahrens und Auswirkungen auf die Leistungsfähigkeit. Kassel: Kassel Univ. Press. Schriftreihe des Fachgebietes Siedlungswasserwirtschaft, Wasser-Abwasser-Umwelt, Bd. 26, Dissertation.

Wiesmann, U., Choi, I. S., Dombrowska, E. M. (2006) Fundamentals of Biological Wastewater Treatment. Wiley VCH Verlag GmbH.

Wozniak, T., Baumgarten, S. (2001) Zweijährige Betriebserfahrungen mit der Membrantechnik in der Kläranlage Büchel. Begleitbuch zur 4. Aachener Tagung Siedlungswasserwirtschaft und Verfahrenstechnik, Aachen.

Wulf, P., Orth, H. (2008) Deckschichtkontrolle und Steigerung der Filtrationsleistung beim Membranbelebungsverfahren durch fluidisierte Reinigungselemente. GWF-Wasser/Abwasser 149(6), pp. 517-521.

Zhang, Z., Gao, J., Zhang, W., Ren, Z. (2006) Experimental Study of the Effect of Membrane Porosity on Membrane Absorption Process. Separation Science and Technology 41(14), pp. 3245-3263.

Zhang, J., Chua, H. C., Zhou, J., Fane, A. G. (2006) Factors affecting the membrane performance in submerged membrane bioreactors. Journal of Membrane Science 284(1-2), pp. 54-66.

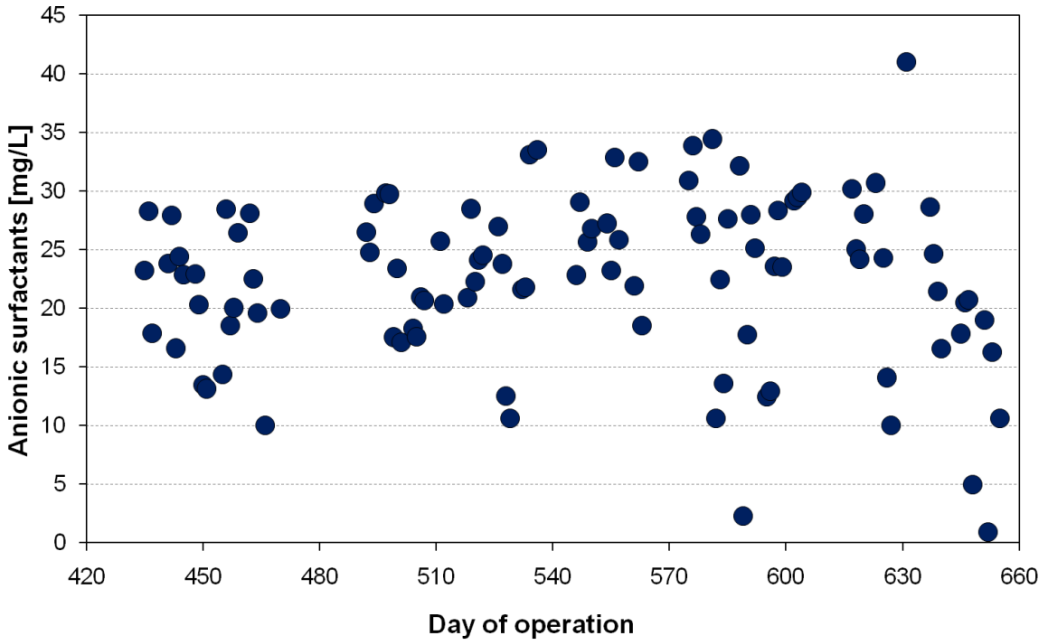
Zhu, X., Elimelech, M. (1995) Fouling of reverse osmosis membranes by aluminium oxide colloids. Journal of Environmental Engineering 121(12), pp. 884-892.

Microdyn-Nadir. Product catalog. http://www.microdyn-nadir.de/cms/pdf/ produkte/en/5_biocel_4s_en_screen.pdf. Accessed May 18, 2010.

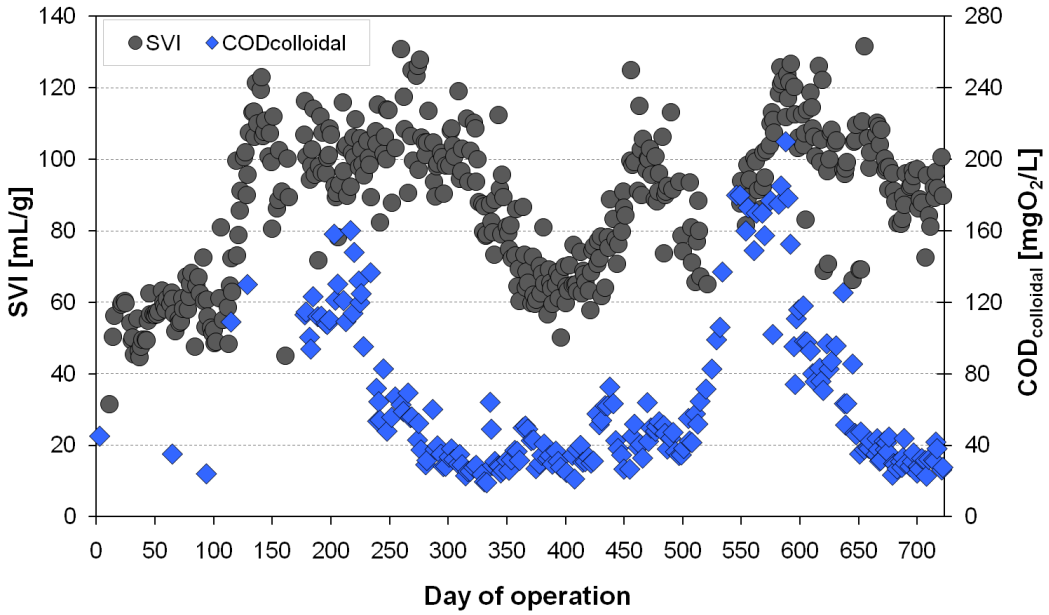
APPENDIX

Appendix A: MBR pilot plant (A) in Darmstadt-Eberstadt

A.1 Overview of investigated parameters over operating time

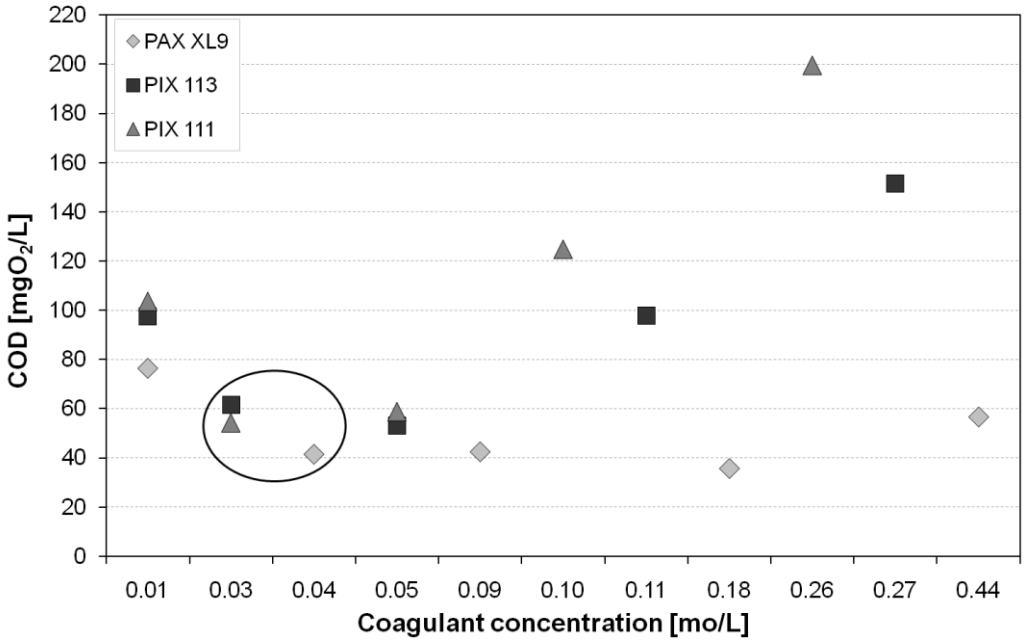


Appendix Figure 1: Trend of anionic surfactants concentration over the investigation period.

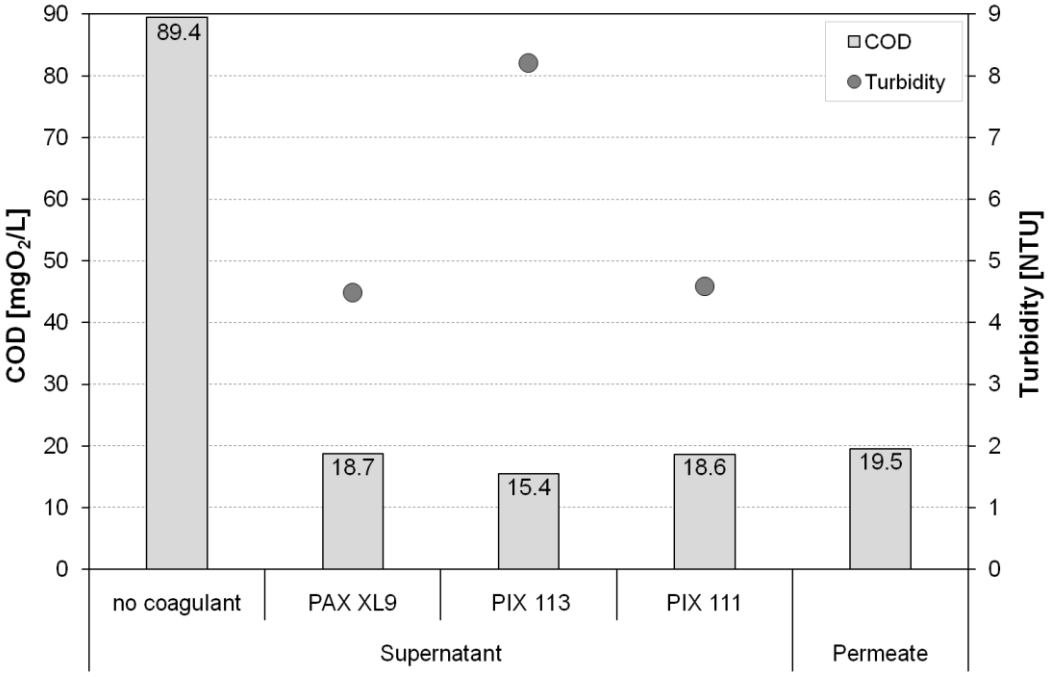


Appendix Figure 2: Trend of colloidal COD concentration and sludge volume index (SVI) over the investigation period.

A.2 Jar test – determination of coagulant and its optimum dose



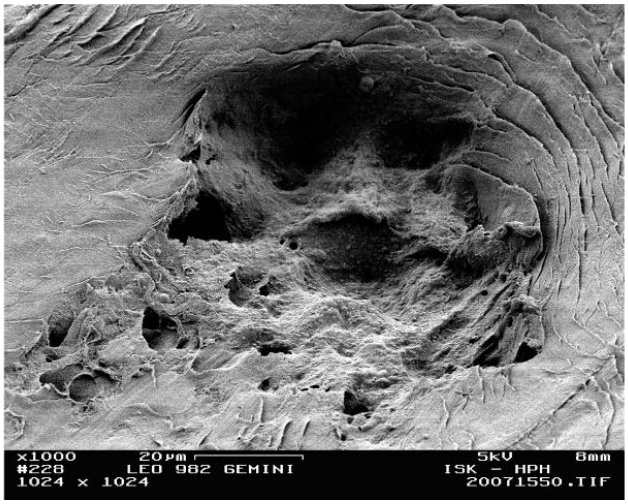
Appendix Figure 3: Determination of the optimum coagulant dose. COD concentration of an untreated supernatant sample was 132 mgO_2/L.

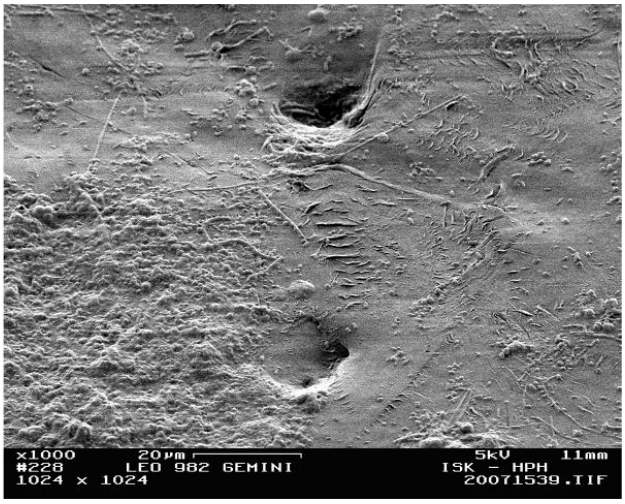


Appendix Figure 4: Effect of coagulants on COD concentration and turbidity. Coagulant dose was 0.04 mol/L.

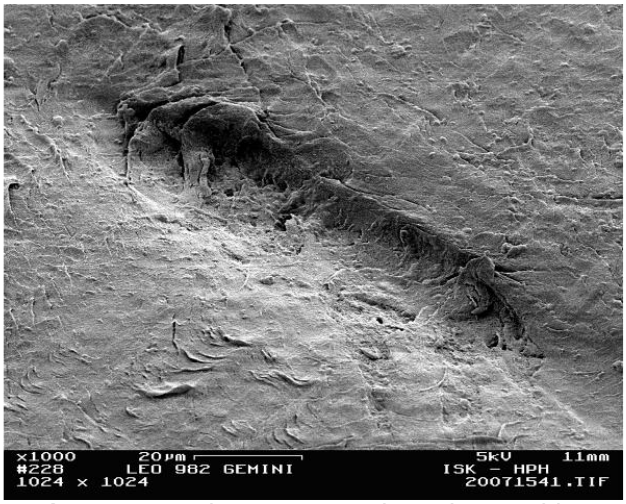
Appendix B: MBR pilot plant (B) in Wiesbaden-Biebrich

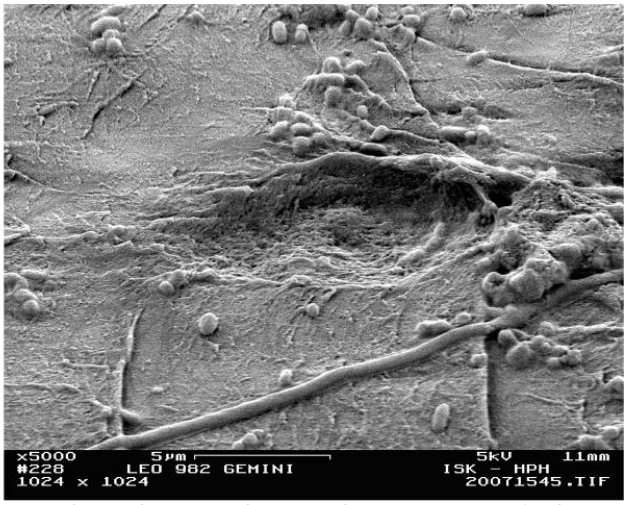
B.1 SEM images - test phase I

a) 

b) 

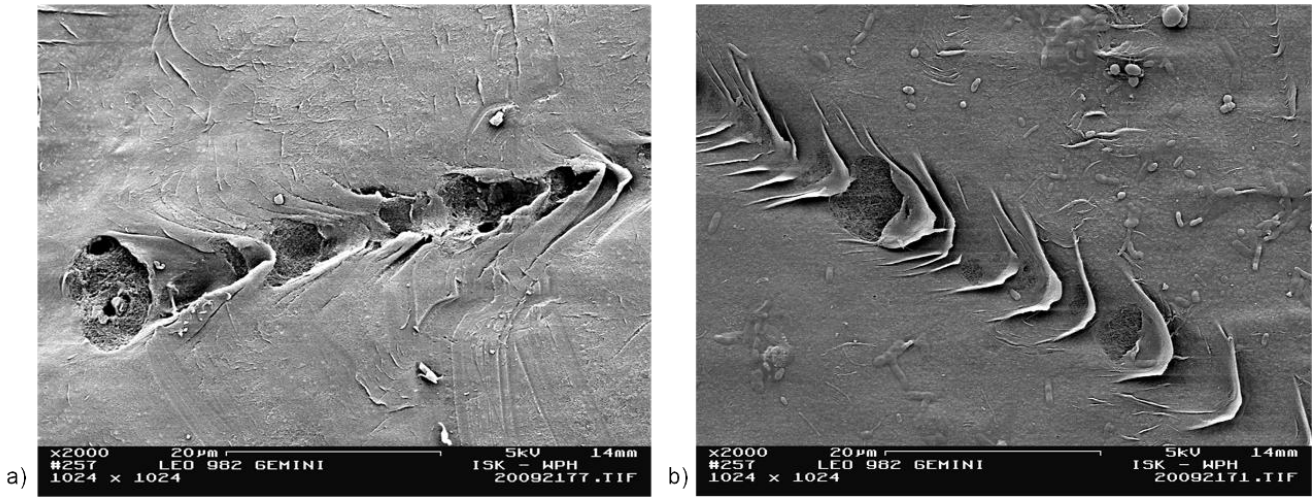
Appendix Figure 5: a) TPU granulate, sheet A; b) PMMA granulate, sheet A. The samples were magnified 1000 times.

a) 

b) 

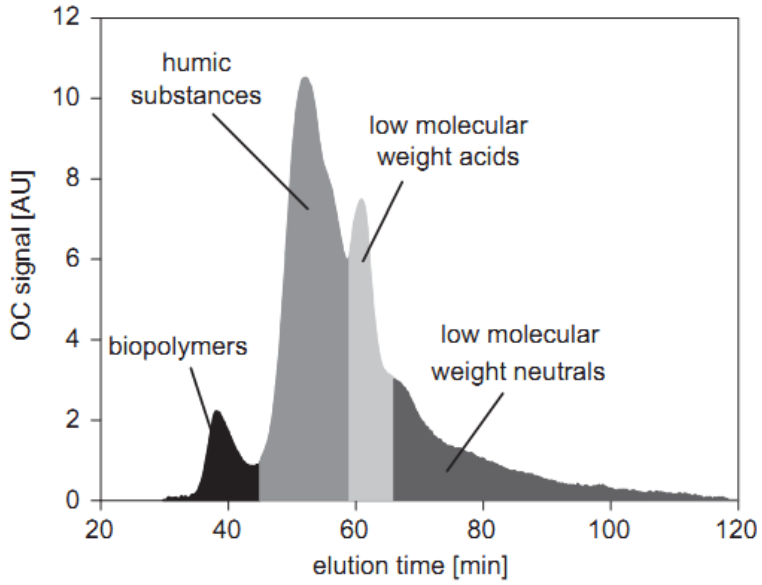
Appendix Figure 6: a) PMMA granulate, sheet A; b) PMMA granulate, sheet A. The samples were magnified 1000 and 5000 times.

B.2 SEM images - test phase II

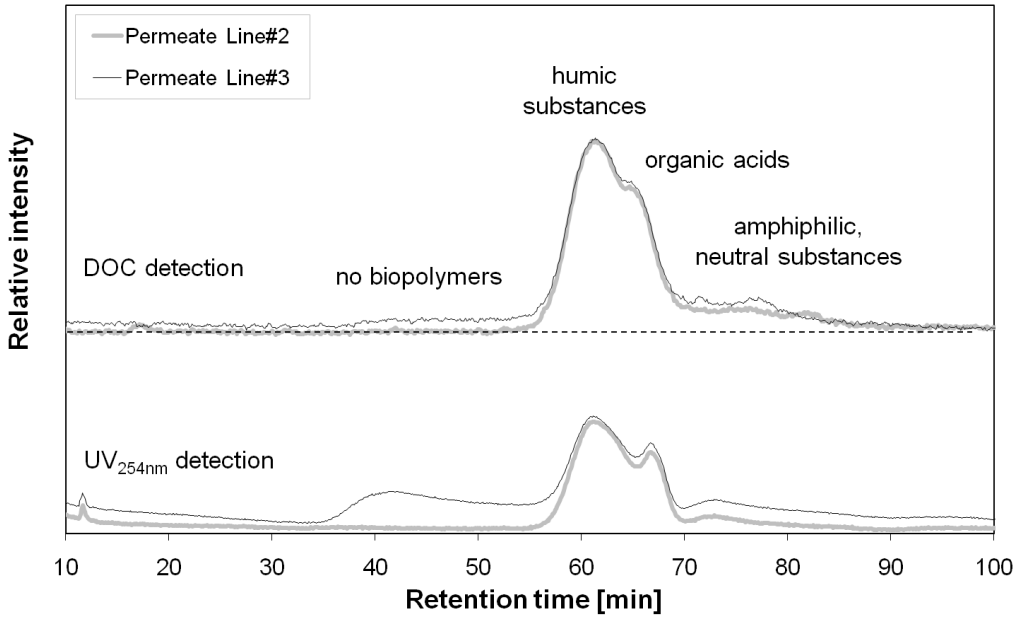


Appendix Figure 7: a) Granulate line; b) reference line. The samples were magnified 2000 times.

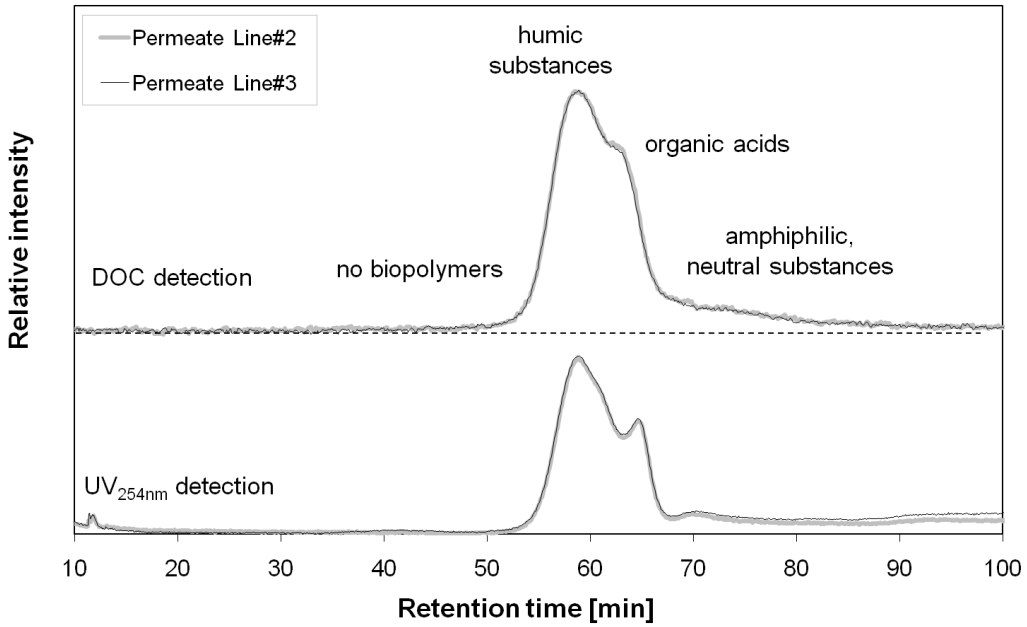
B.3 Size exclusion chromatography/LC-OCD - truly soluble matter (< 0.04 µm)



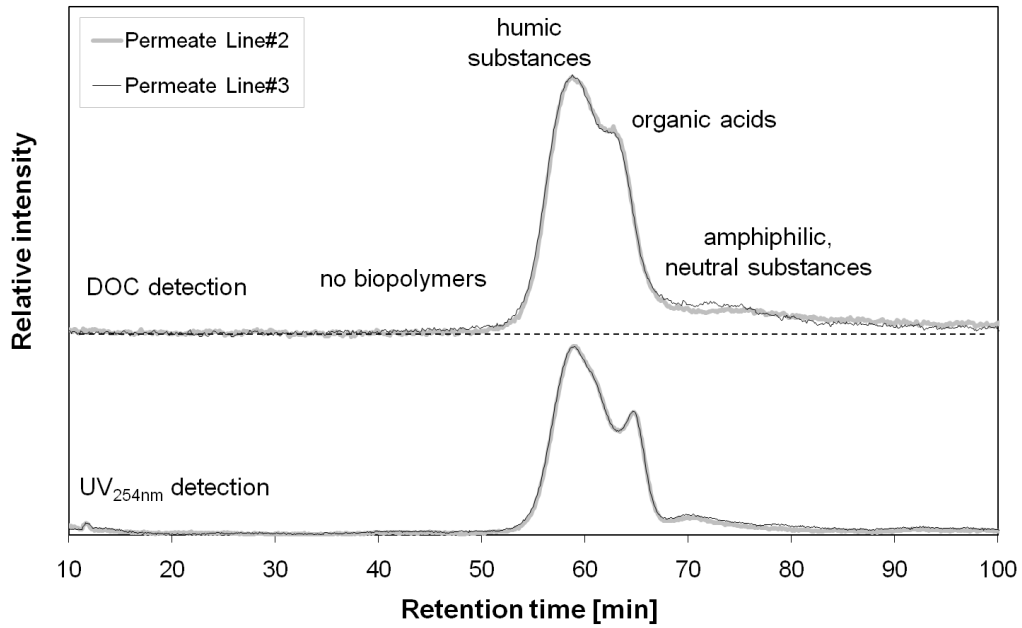
Appendix Figure 8: LC-OCD chromatogram of secondary effluent (*Haberkamp et al., 2007*).



Appendix Figure 9: LC-OCD chromatogram of collected samples (permeate of line#2 and line#3), taken in the 196th day of operation.



Appendix Figure 10: LC-OCD chromatogram of collected samples (permeate of line#2 and line#3), taken in the 267th day of operation.

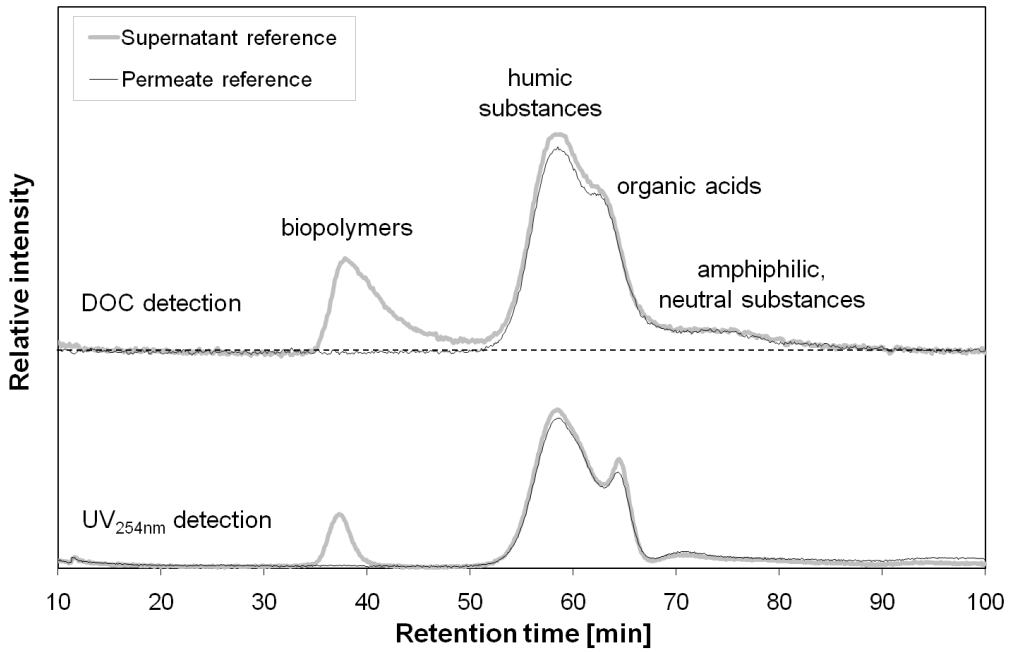


Appendix Figure 11: LC-OCD chromatogram of collected samples (permeate of line#2 and line#3), taken in the 281st day of operation.

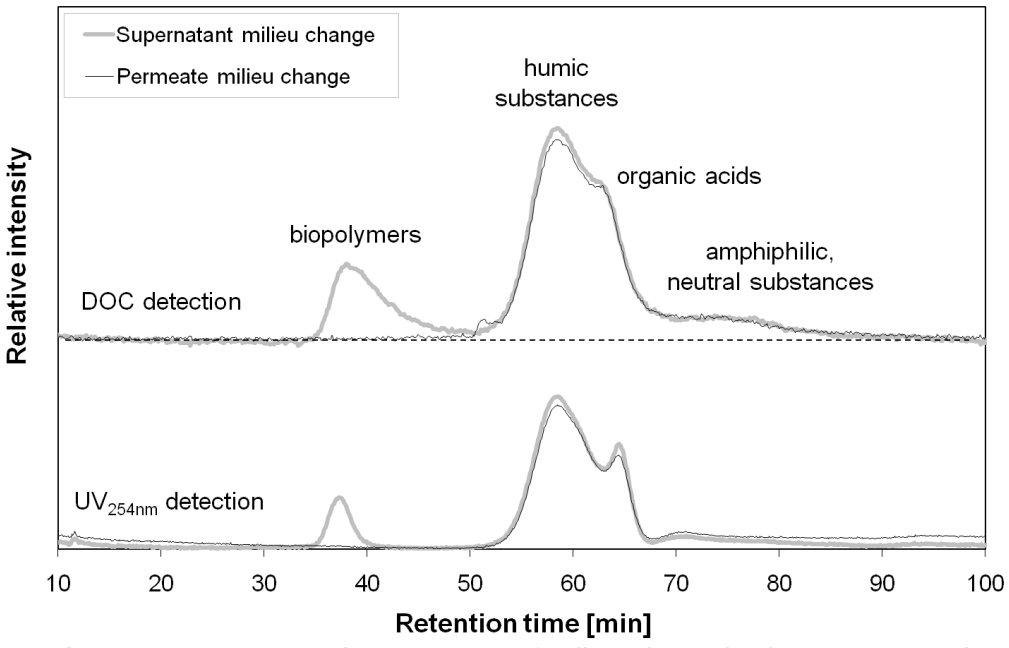
Appendix Table 1: DOC_{total} and DOC of biopolymers of permeate samples (line#1, #2, and #3) taken on the 196th, the 267th, and the 281st day of operation.

Sample	DOC_{total} [mg/L]	DOC of biopolymers [mg/L]	DOC of biopolymers [%]
The 196th day of operation			
Permeate#2	3.73	0.19	5.1
Permeate#3	3.24	0.04	1.4
The 267th day of operation			
Permeate#1 and #2	3.72	0.13	3.5
Permeate#3	3.52	0.11	3.2
The 281st day of operation			
Permeate#1 and #2	4.20	0.11	2.7
Permeate#3	4.09	0.05	1.3

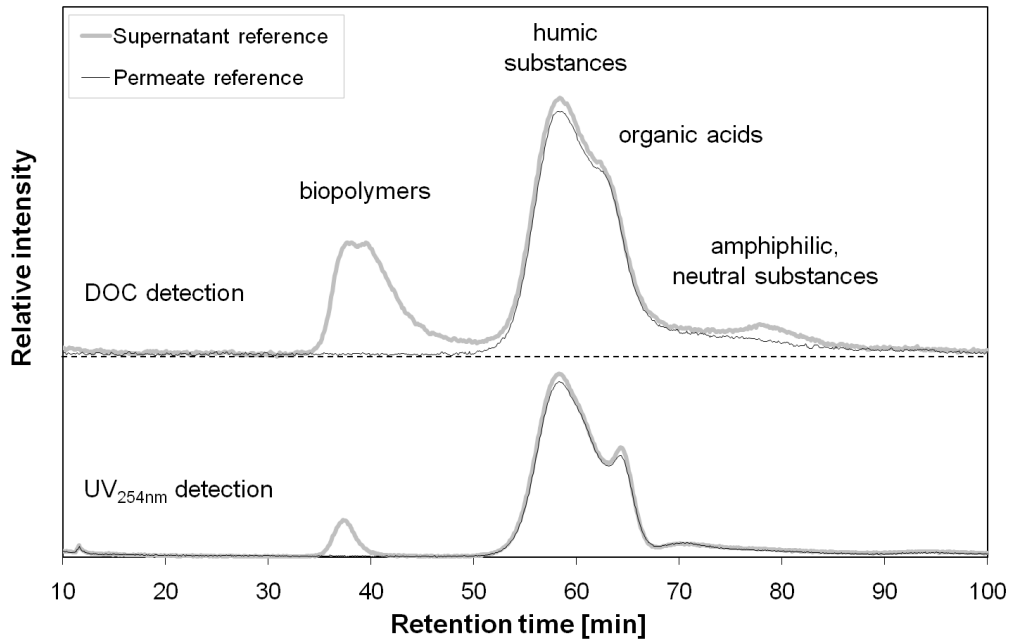
B.4 Size exclusion chromatography/LC-OCD - Change in ambient conditions (aerobic/anaerobic)



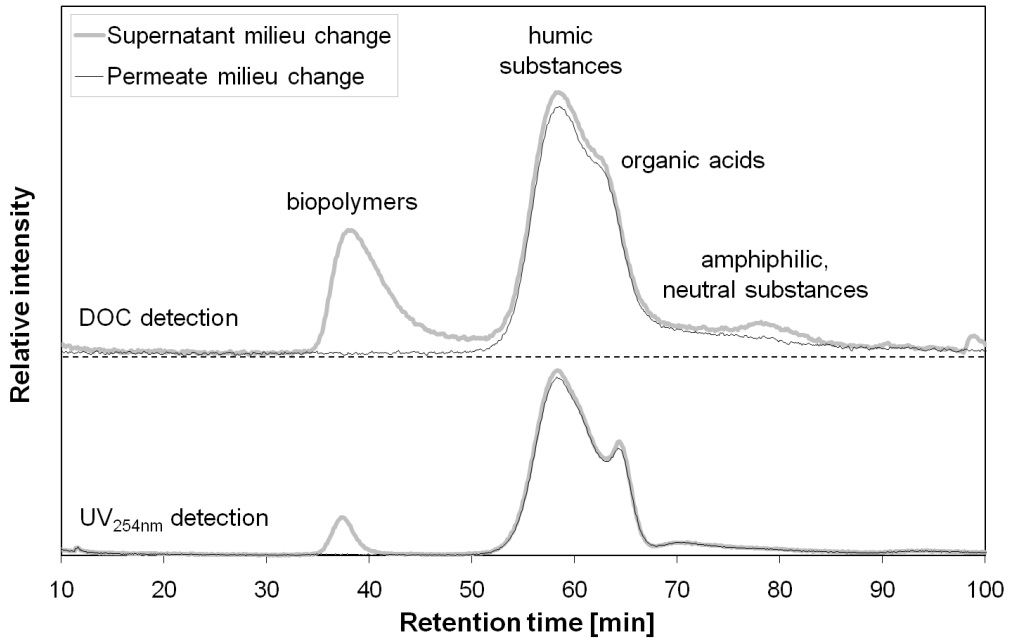
Appendix Figure 12: LC-OCD chromatogram of collected samples (supernatant and permeate of reference line), taken on the 365th day of operation.



Appendix Figure 13: LC-OCD chromatogram of collected samples (supernatant and permeate of milieu change line), taken on the 365th day of operation.



Appendix Figure 14: LC-OCD chromatogram of collected samples (supernatant and permeate of reference line), taken on the 379th day of operation.



Appendix Figure 15: LC-OCD chromatogram of collected samples (supernatant and permeate of milieu change line), taken on the 379th day of operation.

Appendix C: Overview of investigated parameters in glass basin

C.1 Coarse-bubble crossflow system – clean water tests

Coarse-bubble crossflow system		Clean water tests on oxygen transfer					
Test No.	**1**				Date:	25.04.07	
					Time:	12:00	
Air pressure [mbar]:	Start:	997.6	Finish:	997.6	Mean value:	997.6	
Pressure at the crossfow [mbar]:	Start:	154	Finish:	154	Mean value:	154	
Intake air temperature [°C]:	Start:	21.96	Finish:	22.08	Mean value:	22.38	
Test tank							
Volume [m³]:		3					
Water temperature [°C]:		14.02	Immersion depth [m]:			1.45	
Air volume flow [m³/h at STP]:		20.23	spec. air volume flow [m³/m³·h at STP]:			6.7	

O_2 sensor	$k_L a_T$ [1/h]	c_s [mg/L]	$k_L a_{20}$ [1/h]	SOTR [kg/h]	SSOTE [%/m]	SSOTR [g/m³·m] at STP	SAE_{gross} [kg/kWh]
1	8.32	10.9	9.59	0.28	3.19	9.54	2.12
2	8.27	10.35	9.53	0.28	3.17	9.49	2.11
3	8.42	10.74	9.71	0.28	3.23	9.66	2.15
Mean value:	**8.34**	**10.66**	**9.61**	**0.28**	**3.20**	**9.56**	**2.13**
SD	0.08	0.28	0.09	0.00	0.03	0.09	0.02

Coarse-bubble crossflow system		Clean water tests on oxygen transfer					
Test No.	**2**				Date:	26.04.07	
					Time:	11:30	
Air pressure [mbar]:	Start:	998.6	Finish:	998.6	Mean value:	998.6	
Pressure at the crossfow [mbar]:	Start:	164	Finish:	164	Mean value:	164	
Intake air temperature [°C]:	Start:	24.6	Finish:	25.6	Mean value:	25.1	
Test tank							
Volume [m³]:		3					
Water temperature [°C]:		14.2	Immersion depth [m]:			1.45	
Air volume flow [m³/h at STP]:		40.51	spec. air volume flow [m³/m³·h at STP]:			13.5	

O_2 sensor	$k_L a_T$ [1/h]	c_s [mg/L]	$k_L a_{20}$ [1/h]	SOTR [kg/h]	SSOTE [%/m]	SSOTR [g/m³·m] at STP	SAE_{gross} [kg/kWh]
1	17.35	10.49	19.91	0.58	3.31	9.89	2.20
2	17.47	10.38	20.05	0.58	3.33	9.96	2.21
3	17.47	10.38	20.05	0.58	3.33	9.96	2.21
Mean value:	**17.43**	**10.42**	**20.00**	**0.58**	**3.32**	**9.94**	**2.21**
SD	0.07	0.06	0.08	0.00	0.01	0.04	0.01

Coarse-bubble crossflow system **Clean water tests on oxygen transfer**

Test No. **3** Date: 26.04.07
Time: 14:30

Air pressure [mbar]:	Start:	998.6	Finish:	998.6	Mean value:	998.6
Pressure at the crossfow [mbar]:	Start:	168	Finish:	168	Mean value:	168
Intake air temperature [°C]:	Start:	26.5	Finish:	27.9	Mean value:	27.2

Test tank

Volume [m³]:	3		
Water temperature [°C]:	13.6	Immersion depth [m]:	1.45
Air volume flow [m³/h at STP]:	58.35	spec. air volume flow [m³/m³·h at STP]:	19.5

O_2 sensor	k_La_T [1/h]	c_s [mg/L]	k_La_{20} [1/h]	SOTR [kg/h]	SSOTE [%/m]	SSOTR [g/m³·m] at STP	SAE_{gross} [kg/kWh]
1	25.61	10.40	29.81	0.87	3.44	10.28	2.28
2	25.71	10.28	29.92	0.87	3.45	10.32	2.29
3	-	-	-	-	-	-	-
Mean value:	**25.66**	**10.34**	**29.87**	**0.87**	**3.45**	**10.30**	**2.29**
SD	0.07	0.08	0.08	0.00	0.01	0.03	0.01

Coarse-bubble crossflow system **Clean water tests on oxygen transfer**

Test No. **4** Date: 27.04.07
Time: 13:30

Air pressure [mbar]:	Start:	1003	Finish:	1003	Mean value:	1003
Pressure at the crossfow [mbar]:	Start:	181	Finish:	181	Mean value:	181
Intake air temperature [°C]:	Start:	23	Finish:	23.3	Mean value:	23.15

Test tank

Volume [m³]:	3		
Water temperature [°C]:	13.50	Immersion depth [m]:	1.45
Air volume flow [m³/h at STP]:	82.52	spec. air volume flow [m³/m³·h at STP]:	27.5

O_2 sensor	k_La_T [1/h]	c_s [mg/L]	k_La_{20} [1/h]	SOTR [kg/h]	SSOTE [%/m]	SSOTR [g/m³·m] at STP	SAE_{gross} [kg/kWh]
1	34.99	10.29	40.82	1.19	3.33	9.96	2.21
2	34.79	10.12	40.59	1.18	3.31	9.90	2.20
3	-	-	-	-	-	-	-
Mean value:	**34.89**	**10.21**	**40.71**	**1.19**	**3.32**	**9.93**	**2.21**
SD	0.14	0.12	0.16	0.01	0.01	0.04	0.01

C.2 Fine-bubble crossflow system – clean water tests

Fine-bubble crossflow system Clean water tests on oxygen transfer

Test No.	**1**				Date:	25.09.08	
					Time:	10:00	
Air pressure [mbar]:		Start:	1009.5	Finish:	1009.7	Mean value:	1010
Pressure at the crossfow [mbar]:		Start:	338	Finish:	340	Mean value:	339
Intake air temperature [°C]:		Start:	19.92	Finish:	19.94	Mean value:	19.93

Test tank

Volume [m³]:	3		
Water temperature [°C]:	14.3	Immersion depth [m]:	1.77
Air volume flow [m³/h at STP]:	21.4	spec. air volume flow [m³/m³·h at STP]:	7.1

O_2 sensor	$k_L a_T$	c_s	$k_L a_{20}$	SOTR	SSOTE	SSOTR	SAE_{gross}
	[1/h]	[mg/L]	[1/h]	[kg/h]	[%/m]	[g/m³·m] at STP	[kg/kWh]
1	21.15	9.70	24.21	0.72	6.32	18.89	4.12
2	20.61	9.53	23.59	0.70	6.16	18.41	4.09
3	21.03	9.75	24.07	0.71	6.28	18.79	4.18
Mean value:	**20.93**	**9.66**	**23.96**	**0.71**	**6.25**	**18.7**	**4.16**
SD	0.28	0.12	0.32	0.01	0.08	0.25	0.06

Fine-bubble crossflow system Clean water tests on oxygen transfer

Test No. **2** Date: 25.09.08 Time: 10:00

Air pressure [mbar]:	Start:	1010	Finish:	1010.1	Mean value:	1010
Pressure at the crossfow [mbar]:	Start:	371	Finish:	374	Mean value:	372.5
Intake air temperature [°C]:	Start:	22.18	Finish:	27.08	Mean value:	24.63

Test tank

Volume [m³]: 3

Water temperature [°C]: 14.3 Immersion depth [m]: 1.77

Air volume flow [m³/h at STP]: 39.67 spec. air volume flow [m³/m³·h at STP]: 13.2

O_2 sensor	$k_L a_T$	c_s	$k_L a_{20}$	SOTR	SSOTE	SSOTR	SAE_{gross}
	[1/h]	[mg/L]	[1/h]	[kg/h]	[%/m]	[g/m³·m] at STP	[kg/kWh]
1	42.23	9.63	48.34	1.43	6.82	20.38	4.53
2	40.89	9.58	46.81	1.39	6.60	19.73	4.39
3	41.93	9.74	47.99	1.42	6.77	20.24	4.50
Mean value:	**41.68**	**9.65**	**47.72**	**1.41**	**6.73**	**20.12**	**4.47**
SD	0.7	0.08	0.81	0.02	0.11	0.34	0.08

Fine-bubble crossflow system Clean water tests on oxygen transfer

Test No. **3** Date: 25.09.08 Time: 10:00

Air pressure [mbar]:	Start:	1010.5	Finish:	1010.7	Mean value:	1011
Pressure at the crossfow [mbar]:	Start:	397	Finish:	399	Mean value:	398
Intake air temperature [°C]:	Start:	28	Finish:	31.3	Mean value:	29.6

Test tank

Volume [m³]: 3

Water temperature [°C]: 14.3 Immersion depth [m]: 1.77

Air volume flow [m³/h at STP]: 62.02 spec. air volume flow [m³/m³·h at STP]: 20.7

O_2 sensor	$k_L a_T$	c_s	$k_L a_{20}$	SOTR	SSOTE	SSOTR	SAE_{gross}
	[1/h]	[mg/L]	[1/h]	[kg/h]	[%/m]	[g/m³·m] at STP	[kg/kWh]
1	62.01	9.73	71.07	2.10	6.41	19.16	4.26
2	61.86	9.59	70.90	2.10	6.39	19.12	4.25
3	63.03	9.73	72.24	2.14	6.51	19.48	4.33
Mean value:	**62.3**	**9.68**	**71.40**	**2.11**	**6.44**	**19.25**	**4.28**
SD	0.64	0.08	0.73	0.02	0.07	0.20	0.04

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*WA*R 35	Erkundung und Bewertung von Altlasten -Kriterien und Untersuchungsprogramme-. 15. Wassertechnisches Seminar am 12.10.1988, TH Darmstadt, 1989	vergriffen
*WA*R 36	Bestimmung des Sauerstoffzufuhrvermögens von Belüftungssystemen in Reinwasser und unter Betriebsbedingungen. Workshop am 15. u. 16.03.1988, TH Darmstadt, 1989	vergriffen
*WA*R 37	Belüftungssysteme in der Abwassertechnik - Fortschritte und Perspektiven -. 16. Wassertechnisches Seminar am 10.11.1988, TH Darmstadt, 1989	vergriffen
*WA*R 38	Farinha, Joao António Muralha Ribeiro: Die stufenweise Versorgung mit Anlagen der Technischen Infrastruktur in Abhängigkeit von der Entwicklung der sozioökonomischen Verhältnisse der Bevölkerung - dargestellt am Beispiel der Bairros Clandestinos der Region Lissabon-. Dissertation, FB 13, TH Darmstadt, 1989	vergriffen

WAR 39	Sicherstellung der Trinkwasserversorgung Maßnahmen und Strategien für einen wirksamen Grundwasserschutz zur langfristigen Erhaltung der Grundwassergewinnung. 17. Wassertechnisches Seminar am 01.06.1989, TH Darmstadt, 1989	33,20 €
WAR 40	Regenwassernutzung in privaten und öffentlichen Gebäuden -Qualitative und quantitative Aspekte, technische Anlagen-. Studie für den Hessischen Minister für Umwelt und Reaktorsicherheit. TH Darmstadt, 1981	vergriffen
WAR 41	Folgenutzen kontaminierter Betriebsflächen unter besonderer Berücksichtigung der Sanierungsgrenzen. 18. Wassertechnisches Seminar am 11.10.1989, TH Darmstadt, 1989	vergriffen
WAR 42	Privatisierung öffentlicher Abwasseranlagen -Ein Gebot der Stunde ? 19. Wassertechnisches Seminar am 09.11.1989, TH Darmstadt, 1989	30,70 €
WAR 43	Pöpel, H. Johannes; Joachim Glasenapp; Holger Scheer: Planung und Betrieb von Abwasserreinigungsanlagen zur Stickstoffelimination. Gutachten für das Hess. Ministerium für Umwelt und Reaktorsicherheit, TH Darmstadt, 1990	35,80 €
WAR 44	Abfallentsorgung Hessen. Standpunkte - Gegensätze - Perspektiven Abfallwirtschaftliches Symposium am 31.10.1989, TH Darmstadt, 1990	30,70 €
WAR 45	Brettschneider, Uwe: Die Bedeutung von Sulfaten in der Siedlungswasserwirtschaft und ihre Entfernung durch Desulfurikation. Dissertation, FB 13, TH Darmstadt, 1990	vergriffen
WAR 46	Grabenlose Verlegung und Erneuerung von nicht begehbaren Leitungen -Verfahren, Anwendungsgrenzen, Erfahrungen und Perspektiven-. 20. Wassertechnisches Seminar am 29.03.1990, TH Darmstadt, 1990	35,80 €
WAR 47	Härtel, Lutz: Modellansätze zur dynamischen Simulation des Belebtschlammverfahrens. Dissertation, FB 13, TH Darmstadt, 1990	vergriffen
WAR 48	Pflanzenkläranlagen - besser als ihr Ruf? 21. Wassertechnisches Seminar am 18.09.1990, TH Darmstadt, 1990	vergriffen
WAR 49	Umweltverträglichkeitsprüfung (UVP) in der Wasserwirtschaft - administrativer Wildwuchs oder ökologische Keule? Dokumentation der Beiträge zum Interdisziplinären Kolloquium am 23.02.1990 und zum Sachverständigengespräch am 23.02.1990, TH Darmstadt, 1991	vergriffen
WAR 50	UVP in der abfallwirtschaftlichen Planung. 22. Wassertechnisches Seminar am 18.10.1990, TH Darmstadt, 1991	vergriffen
WAR 51	Biologische und chemische Phosphatelimination - Technische Möglichkeiten und Grenzen -. 23. Wassertechnisches Seminar am 15.11.1990, TH Darmstadt, 1991	35,80 €

*WA*R 52	Pöpel, H. Johannes; Tankred Börner: Wurzelraum-Modellanlage Hofgeismar-Beberbeck -Pilotprojekt des Landes Hessen. Gutachten für das Hess. Ministerium für Umwelt und Reaktorsicherheit. TH Darmstadt, 1991	vergriffen
*WA*R 53	Wagner, Martin: Einfluß oberflächenaktiver Substanzen auf Stoffaustauschmechanismen und Sauerstoffeintrag. Dissertation, FB 13, TH Darmstadt, 1991	35,80 €
*WA*R 54	Belüftungssysteme in der Abwassertechnik 1991 - Fortschritte und Perspektiven -. 1. gemeinsames Abwassertechnisches Seminar mit der Hochschule für Architektur und Bauwesen Weimar am 11. und 12.04. 1991 in Weimar, TH Darmstadt, 1991	30,70 €
*WA*R 55	Neuere gesetzliche Anforderungen und moderne technische Lösungen zur Sicherung der Wasserversorgung - Erkennen, Vermeiden und Beseitigen von Schadstoffen - 24. Wassertechnisches Seminar am 16.05.1991 TH Darmstadt, 1991	vergriffen
*WA*R 56	Zhang, Jiansan: Energiebilanzierung anaerob-mesophiler Stabilisierungsanlagen mit vorgeschalteter aerob-thermophiler Stufe Dissertation, FB 13, TH Darmstadt, 1991	vergriffen
*WA*R 57	Glasenapp, Joachim: Leistungsfähigkeit und Wirtschaftlichkeit von Verfahrensvarianten zur Sickstoffelimination beim Belebtschlammverfahren. Dissertation, FB 13, TH Darmstadt, 1992	vergriffen
*WA*R 58	Börner, Tankred: Einflußfaktoren für die Leistungsfähigkeit von Pflanzenkläranlagen. Dissertation, FB 13, TH Darmstadt, 1992	vergriffen
*WA*R 59	Erzmann, Michael: Untersuchungen zur biologischen Elimination von chlorierten Lösemitteln aus Abwasser. Dissertation, FB 13, TH Darmstadt, 1992	35,80 €
*WA*R 60	Erfassung und Sanierung schadhafter Abwasserkanäle. 26. Wassertechnisches Seminar am 28.11.1991 TH Darmstadt, 1992	35,80 €
*WA*R 61	Realisierung von Entsorgungsanlagen Umsetzungsprobleme und Lösungsansätze aus planerischer, verwaltungsrechtlicher und politischer Sicht. 25. Wassertechnisches Seminar am 07.11.1991, TH Darmstadt, 1992	vergriffen
*WA*R 62	Koziol, Matthias: Umwelteffekte durch Förderung von Energieeinsparmaßnahmen in innerstädtischen Althausgebieten. Dissertation, FB 13, TH Darmstadt, 1992	25,60 €
*WA*R 63	Lautner, Gerd: Einführung in das Bauordnungsrecht. 7. erw. Auflage TH Darmstadt, 1992	vergriffen

WAR 64	Abwasserkanäle - Bemessung, Ausführung, Sanierung - 2. gemeinsames Seminar -Abwassertechnik- mit der Hochschule für Architektur und Bauwesen Weimar am 18. und 19.03.1992 in Weimar, TH Darmstadt, 1992	vergriffen
WAR 65	Optimierung der Grundwassergewinnung über Filterbrunnen Neue Bau- und Betriebserkenntnisse - 27. Wassertechnisches Seminar am 21.05.1992, TH Darmstadt, 1992	vergriffen
WAR 66	Kläschlammbehandlung und Klärschlammentsorgung -Stand und Entwicklungstendenzen- 31. Darmstädter Seminar -Abwassertechnik- am 12.11.1992, TH Darmstadt, 1992	35,80 €
WAR 67	Kreislaufwirtschaft Bau - Stand und Perspektiven beim Recycling von Baurestmassen- 32. Darmstädter Seminar -Abfalltechnik- am 09.03.1993, TH Darmstadt, 1993	30,70 €
WAR 68	Bewertung von Geruchsemissionen und -immissionen 29. Darmstädter Seminar -Immissionsschutz- am 08.10.1992, TH Darmstadt, 1993	25,60 €
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WAR 70	Sichere Wasserversorgung durch moderne Rohrleitungstechnik 33. Darmstädter Seminar -Wasserversorgungstechnik- am 11.03.1993, TH Darmstadt, 1993	30,70 €
WAR 71	Aktuelle Aufgaben der Abwasserreinigung und Schlammbehandlung 35. Darmstädter Seminar -Abwassertechnik- am 05. + 06.05.1993, TH Darmstadt, 1993	46,-- €
WAR 72	Raumordnungsverfahren mit Umweltverträglichkeitsprüfung und Umweltleitbilder für die Landes- und Regionalplanung 28. und 30. Darmstädter Seminar -Raumplanung- am 17.09. + 05.11.1992, TH Darmstadt, 1993	40,90 €
WAR 73	Grohmann, Walter: Vergleichende Untersuchungen von Belüftungs- und Durchmischungssystemen zur bioverfahrenstechnischen Optimierung der aerob-thermophilen Stabilisation (ATS). Dissertation, FB 13, TH Darmstadt, 1993	35,80 €
WAR 74	Dioxinimmissionen und Quellen 34. Darmstädter Seminar -Immissionsschutz- am 15.04.1993, TH Darmstadt, 1994	30,70 €
WAR 75	Betrieb von Abwasserbehandlungsanlagen Optimierung, Prozeßstabilität, Kosteneinsparung 36. Darmstädter Seminar -Abwassertechnik- am 04.11.1993 in Darmstadt und 5. gemeinsames Seminar -Abwassertechnik- mit der Fakultät Bauingenieurwe-sen der Hochschule für Architektur und Bauwesen Weimar am 23. und 24.03.1994 in Weimar, TH Darmstadt, 1994	46,-- €

*WA*R 76	Umweltgerechte Ausweisung und Erschließung von Gewerbegebieten 4. gemeinsames Seminar -Umwelt- und Raumplanung- mit der Fakultät Architektur, Stadt- und Regionalplanung der Hochschule für Architektur und Bauwesen Weimar am 08. und 09.09.1993 in Weimar, TH Darmstadt, 1994	vergriffen
*WA*R 77	Von der Umweltverträglichkeitsprüfung zum kooperativen Planungsmanagement. -Das Scoping-Verfahren als erste Stufe!?- 37. Darmstädter Seminar -Umwelt- und Raumplanung- am 11.11.1993, TH Darmstadt, 1994	vergriffen
*WA*R 78	Modellbildung und intelligente Steuerungssysteme in der Umwelttechnik. 38. Darmstädter Seminar -Abfalltechnik- am 24.02.1994, TH Darmstadt, 1994	vergriffen
*WA*R 79	Brauchwassernutzung in Haushalten und Gewerbebetrieben - Ein Gebot der Stunde? 39. Darmstädter Seminar -Wasserversorgungstechnik- am 17.03.1994, TH Darmstadt, 1994	25,60 €
*WA*R 80	Restabfallbehandlung in Hessen 41. Darmstädter Seminar -Abfalltechnik- mit dem Hessischen Ministerium für Umwelt, Energie und Bundesangelegenheiten -HMUEB- am 16.06.1994, TH Darmstadt, 1994	vergriffen
*WA*R 81	Umweltbeeinflussung durch biologische Abfallbehandlungsverfahren 42. Darmstädter Seminar -Abfalltechnik- mit dem Institut für Hygiene der FU Berlin und dem Institut für Meteorologie der TH Darmstadt am 08. und 09.09.1994 in Berlin, TH Darmstadt, 1994	46,-- €
*WA*R 82	Zeitgemäße Planung von Anlagen der Ortsentwässerung -Kanäle, Bauwerke, Sonderbauwerke- 6. gemeinsames Seminar -Abwassertechnik- mit der Fakultät Bauingenieur-wesen der Hochschule für Architektur und Bauwesen Weimar am 15. und 16.03.1995 in Weimar, TH Darmstadt, 1995	vergriffen
*WA*R 83	Grundwasseranreicherung -Stand der Technik und neuere Entwicklungen- 44. Darmstädter Seminar -Wasserversorgungstechnik- mit dem Verein des Gas- und Wasserfaches e.V. -DVGW- am 26.04.1994, TH Darmstadt, 1995	30,70 €
*WA*R 84	Auswirkungen der Phosphorelimination auf die Schlammbehandlung Theoretische Erkenntnisse und praktische Erfahrungen Workshop vom 24. bis 25. November 1994, TH Darmstadt, 1995	30,70 €
*WA*R 85	Stickstoffelimination mit oder ohne externe Substrate ? - Erfahrungen und Überlegungen - 43. Darmstädter Seminar -Abwassertechnik- in Abstimmung mit der Abwassertechnischen Vereinigung e.V. (ATV) am 09.11.1994, TH Darmstadt, 1995	Vergriffen

WAR 85	Stickstoffelimination mit oder ohne externe Substrate ? - Erfahrungen und Überlegungen - 2. Auflage Wiederholung des 43. Darmstädter Seminars -Abwassertechnik- in Abstimmung mit der Abwassertechnischen Vereinigung e.V. (ATV) am 01.02.1996 in Düsseldorf TH Darmstadt, 1996	35,80 €
WAR 86	Möglichkeiten und Grenzen der Einsparung von Investitions- und Betriebskosten bei der Abwasserbehandlung 47. Darmstädter Seminar -Abwassertechnik- am 15.11.1995, TH Darmstadt, 1995	40,90 €
WAR 87	Jardin, Norbert: Untersuchungen zum Einfluß der erhöhten biologischen Phosphorelimination auf die Phosphordynamik bei der Schlammbehandlung. Dissertation, FB 13, TH Darmstadt, 1996	35,80 €
WAR 88	Thermische Restabfallbehandlung für kleine Planungsräume. 45. Darmstädter Seminar -Abfalltechnik- am 22.06.1995 in Hanau, TH Darmstadt, 1996	35,80 €
WAR 89	Ferber, Uwe: Aufbereitung und Revitalisierung industrieller Brachflächen in den traditionellen Industrieregionen Europas. Sonderprogramme im Vergleich. Dissertation, FB 13, TH Darmstadt 1996	25,60 €
WAR 90	Mechanisch-biologische Restabfallbehandlung unter Einbindung thermischer Verfahren für Teilfraktionen. 48. Darmstädter Seminar -Abfalltechnik- am 29.02.1996, TH Darmstadt, 1996	40,90 €
WAR 91	Neuere Erkenntnisse bei Planung, Bau, Ausrüstung und Betrieb von Abwasserbehandlungsanlagen. 7. gemeinsames Seminar -Abwassertechnik- mit der Fakultät Bauingenieur-wesen der Bauhaus-Universität Weimar am 11. und 12.09.1996 in Weimar, TH Darmstadt, 1996	40,90 €
WAR 92	Hygiene in der Abfallwirtschaft. 50. Darmstädter Seminar -Abfalltechnik- am 17.10.1996, TH Darmstadt, 1996	30,70 €
WAR 93	Europäische Richtlinien und Normen zur Abwassertechnik -Konsequenzen und Folgerungen für die Praxis in Deutschland-. 51. Darmstädter Seminar -Abwassertechnik- am 14.11.1996, TH Darmstadt, 1996	25,60 €
WAR 94	Dickhaut, Wolfgang: Möglichkeiten und Grenzen der Erarbeitung von Umweltqualitätszielkonzepten in kooperativen Planungsprozessen. -Durchführung und Evaluierung von Projekten-. Dissertation, FB 13, TH Darmstadt 1996	30,70 €
WAR 95	Lautner, Gerd: Einführung in das Baurecht. 8. erweiterte und aktualisierte Auflage, TH Darmstadt, 1997	15,40 €
WAR 96	Reichert, Joachim: Bilanzierung des Sauerstoffeintrags und des Sauerstoffverbrauchs mit Hilfe der Abluftmethode. Dissertation, FB 13, TH Darmstadt 1997	46,-- €

*WA*R 97	Kuchta, Kerstin: Produktion von Qalitätsgütern in der Abfallbehandlung. Dargestellt am Beispiel der Produktion in der thermischen Abfallbehandlung. Dissertation, FB 13, TH Darmstadt 1997	30,70 €
*WA*R 98	Görg, Horst: Entwicklung eines Prognosemodells für Bauabfälle als Baustein von Stoffstrom-betrachtungen zur Kreislaufwirtschaft im Bauwesen. Dissertation, FB 13, TH Darmstadt, 1997	46,-- €
*WA*R 99	Tiebel-Pahlke, Christoph: Abfallentsorgungsplanung – Beeinflussung der Umweltauswirkungen von Deponien. Dissertation, FB 13, TH Darmstadt, 1997	30,70 €
*WA*R 100	Wagner, Martin: Sauerstoffeintrag und Sauerstoffertrag von Belüftungssystemen und deren Bestimmung mit modernen Meßmethoden. Habilitation, FB 13, TH Darmstadt, 1997	vergriffen
*WA*R 101	Neue Trends bei der Behandlung und Entsorgung kommunaler und industrieller Klärschlämme. 8. gemeinsames Seminar -Abwassertechnik- mit der Fakultät Bauingenieur-wesen der Bauhaus-Universität Weimar am 10. und 11.09.1997 in Weimar, TH Darmstadt, 1997	35,80 €
*WA*R 102	Senkung der Betriebskosten von Abwasserbehandlungsanlagen. 52. Darmstädter Seminar -Abwassertechnik- am 06.11.1997 in Darmstadt, TU Darmstadt, 1997	35,80 €
*WA*R 103	Sanierung und Rückbau von Bohrungen, Brunnen und Grundwassermessstellen. 53. Darmstädter Seminar -Wasserversorgung- am 13.11.1997 in Darmstadt mit dem Deutschen Verein des Gas- und Wasserfaches e.V. – DVGW-, TU Darmstadt, 1997	30,70 €
*WA*R 104	Wünschmann, Gabriele: Untersuchungen zur Kompostierbarkeit von Reststoffen der Papierindustrie und Altpapier unter besonderer Berücksichtigung von Schadstoffbilanzierungen. Dissertation, FB 13, TU Darmstadt, 1997	25,60 €
*WA*R 105	Mechanisch-biologische Restabfallbehandlung unter Einbindung thermischer Verfahren für Teilfraktionen. 54. Darmstädter Seminar -Abfalltechnik- am 06.02.1998 in Darmstadt mit dem Hessischen Ministerium für Umwelt, Energie, Jugend, Familie und Gesundheit und der Südhessischen Arbeitsgemeinschaft Abfallwirtschaft (SAGA)-. TU Darmstadt, 1998	40,90 €
*WA*R 106	Zentrale oder dezentrale Enthärtung von Trinkwasser – Konkurrenz oder sinnvolle Ergänzung ? 55. Darmstädter Seminar -Wasserversorgung- am 14.05.1998 in Darmstadt mit dem Deutschen Verein des Gas- und Wasserfaches e.V. -DVGW- TU Darmstadt, 1998	35,80 €

*WA*R 107	Dach, Joachim: Zur Deponiegas- und Temperaturentwicklung in Deponien mit Siedlungsabfällen nach mechanisch-biologischer Abfallbehandlung. Dissertation, FB 13, TU Darmstadt, 1998	35,80 €
*WA*R 108	Einsparung von Kosten für Betriebsmittel, Energie und Personal auf Abwasserbehandlungsanlagen. 9. gemeinsames Seminar -Abwassertechnik- am 16. und 17.09.1998 in Weimar mit der Fakultät Bauingenieurwesen der Bauhaus-Universität Weimar, TU Darmstadt, 1998	40,90 €
*WA*R 109	Fortschritte in der Abwassertechnik – 15 Jahre Forschungs- und Entwicklungstätigkeit von Prof. Dr.-Ing. H. Johannes Pöpel. 56. Darmstädter Seminar -Abwassertechnik- am 05.11.1998 in Darmstadt TU Darmstadt, 1998	40,90 €
*WA*R 110	Qualitativer und Quantitativer Grundwasserschutz –Stand und Perspektiven-. 57. Darmstädter Seminar -Wasserversorgung- am 10.06.1999 in Darmstadt mit dem Deutschen Verein des Gas- und Wasserfaches e.V. -DVGW- TU Darmstadt, 1999	35,80 €
*WA*R 111	Schwing, Elke: Bewertung der Emissionen der Kombination mechanisch-biologischer und thermischer Abfallbehandlungsverfahren in Südhessen. Dissertation, FB 13, TU Darmstadt, 1999	30,70 €
*WA*R 112	Schade, Bernd: Kostenplanung zur Analyse der Wirtschaftlichkeit von biologischen Restabfallbehandlungsanlagen. Dissertation, FB 13, TU Darmstadt, 1999	30,70 €
*WA*R 113	Lohf, Astrid: Modellierung der chemisch-physikalischen Vorgänge im Müllbett von Rostfeuerungsanlagen. Dissertation, FB 13, TU Darmstadt, 1999	25,60 €
*WA*R 114	Stackelberg, Daniel von: Biologische Festbettdenitrifikation von Grundwasser mit abbaubarem Trägermaterial. Dissertation, FB 13, TU Darmstadt, 1999	30,70 €
*WA*R 115	Folgerungen aus 10 Jahren Abwasserbeseitigung in den neuen Bundesländern -Erfahrungen und Perspektiven- 10. gemeinsames Seminar –Abwassertechnik- am 01. und 02.09.1999 in Weimar mit der Fakultät Bauingenieurwesen der Bauhaus-Universität Weimar, TU Darmstadt, 1999	40,90 €
*WA*R 116	Abwasserwiederverwendung in wasserarmen Regionen - Einsatzgebiete, Anforderungen, Lösungsmöglichkeiten -. 58. Darmstädter Seminar –Abwassertechnik- am 11.11.1999 in Darmstadt, TU Darmstadt, 1999	vergriffen

*WA*R 117	Reinhardt, Tim: Untersuchungen zur Dynamik biologischer Prozesse in drei-Phasen-Systemen am Beispiel der Restabfallrotte unter besonderer Berücksichtigung anaerober Teilprozesse. Dissertation, FB 13, TU Darmstadt, 1999	30,70 €
*WA*R 118	Umweltfachpläne und Umweltgesetzbuch -Ein Beitrag zur Fortentwicklung des Umweltfachplanungssystems- und „Von der Landschaftsplanung zur Umweltleitplanung?“ 46. Darmstädter Seminar -Umwelt- und Raumplanung- am 28.09.1995 in Darmstadt, TU Darmstadt, 1999	30,70 €
*WA*R 119	Herr, Christian: Innovative Analyse und primärseitige Prozeßführungsoptimierung thermischer Abfallbehandlungsprozesse – am Beispiel der Mülleingangsklassifizierung bei der Rostfeuerung. Dissertation, FB 13, TU Darmstadt, 2000	33,20 €
*WA*R 120	Neumüller, Jürgen: Wirksamkeit von Grundwasserabgaben für den Grundwasserschutz – am Beispiel des Bundeslandes Hessen. Dissertation, FB 13, TU Darmstadt, 2000	35,80 €
*WA*R 121	Hunklinger, Ralph: Abfalltechnische Kennzahlen zur umweltgerechten Produktentwicklung. Dissertation, FB 13, TU Darmstadt, 2000	30,70 €
*WA*R 122	Wie zukunftsfähig sind kleinere Wasserversorgungsunternehmen? 60. Darmstädter Seminar -Wasserversorgung- am 29. Juni 2000 in Darmstadt. TU Darmstadt, 2000	35,80 €
*WA*R 123	Massnahmen zur Betriebsoptimierung von Pumpwerken, Kanalisationssystemen und Abwasserbhandlungsanlagen. 11. gemeinsames Seminar -Abwassertechnik- in Weimar am 20. und 21. September 2000 mit der Fakultät Bauingenieurwesen der Bauhaus-Universität Weimar. TU Darmstadt, FB 13, 2000	40,90 €
*WA*R 124	Mohr, Karin: Entwicklung einer on-line Emissionsmeßtechnik zur quasi-kontinuierlichen Bestimmung von Organohalogen-Verbindungen in Abgasen thermischer Prozesse. Dissertation, FB 13, TU Darmstadt, 2000	30,70 €
*WA*R 125	El-Labani, Mamoun: Optimierte Nutzung bestehender Abfallverbrennungsanlagen durch Errichtung vorgeschalteter Reaktoren zur Behandlung heizwertreicher Abfälle. Dissertation, FB 13, TU Darmstadt, 2000	25,60 €
*WA*R 126	Durth, Anke: Einfluß von Temperatur, Anlagenkonfiguration und Auslastung auf die Ablaufkonzentration bei der biologischen Abwasserreinigung. Dissertation, FB 13, TU Darmstadt, 2000	25,60 €
*WA*R 127	Meyer, Ulrich: Untersuchungen zum Einsatz von Fuzzy-Control zur Optimierung der Stickstoffelimination in Abwasserbehandlungsanlagen mit vorgeschalteter Denitrifikation. Dissertation, FB 13, TU Darmstadt, 2000	33,20 €

*WA*R 128	Kommunale Klärschlammbehandlung vor dem Hintergrund der neuen europäischen Klärschlammrichtlinie. 61. Darmstädter Seminar -Abwassertechnik- am 09.11.2000 in Darmstadt, TU Darmstadt, FB 13, 2000	35,80 €
*WA*R 129	Mengel, Andreas: Stringenz und Nachvollziehbarkeit in der fachbezogenen Umweltplanung. Dissertation, FB 13, TU Darmstadt, 2001	46,-- €
*WA*R 130	Kosteneinsparungen durch neuartige Automatisierungstechniken in der Wasserversorgung. 62. Darmstädter Seminar -Wasserversorgung- am 07.06.2001 in Darmstadt, TU Darmstadt, FB 13, 2001	30,70 €
*WA*R 131	Aktive Zukunftsgestaltung durch Umwelt- und Raumplanung. Festschrift zum 60. Geburtstag von Prof. Dr.-Ing. Hans Reiner Böhm. TU Darmstadt, FB 13, 2001	25,60 €
*WA*R 132	Aktuelle Ansätze bei der Klärschlammbehandlung und -entsorgung. 12. gemeinsames Seminar -Abwassertechnik- in Weimar am 05. und 06. September 2001 mit der Fakultät Bauingenieurwesen der Bauhaus-Universität Weimar. TU Darmstadt, FB 13, 2001	40,90 €
*WA*R 133	Zum Bodenwasser- und Stoffhaushalt auf unterschiedlich bewirtschafteten Flächen unter Einbeziehung ökonomischer Aspekte Interdisziplinäre Projektstudie der Technischen Universität Darmstadt (TUD) mit Partner. TU Darmstadt, FB 13, 2001	30,70 €
*WA*R 134	Neues zur Belüftungstechnik - Probleme, Lösungsmöglichkeiten, Entwicklungen - 64. Darmstädter Seminar -Abwassertechnik- am 15.11.2001 in Darmstadt, TU Darmstadt, FB 13, 2001	35,-- €
*WA*R 135	Auswirkungen der Verordnung über die umweltverträgliche Ablagerung von Siedlungsabfällen und über biologische Abfallbehandlungsanlagen. 63. Darmstädter Seminar -Abfalltechnik- am 12. und 13.11.2001 in Darmstadt, TU Darmstadt, FB 13, 2001	35,-- €
*WA*R 136	Bockreis, Anke: Infrarot-Thermographie zur Überwachung von Flächenbiofiltern. Dissertation, FB 13, TU Darmstadt, 2001	35,-- €
*WA*R 137	Luft, Cornelia: Luftgetragene mikrobielle Emissionen und Immissionen an aeroben mechanisch-biologischen Abfallbehandlungsanlagen. Dissertation, FB 13, TU Darmstadt, 2002	30,-- €
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